

Extending the kinetic theory-based thermal conductivity model to reciprocal molten salt mixtures with short-range ordering via the Modified Quasi-chemical Model in the Quadruplet Approximation

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ABSTRACT

Molten salts are among the most promising materials for advanced energy systems in the renewable energy and nuclear fields, with thermal conductivity being a critical property that directly impacts the efficiency of heat transfer processes. However, reliable experimental data on the thermal conductivity for molten salt mixtures is scarce, requiring the use of atomistic simulations and robust theoretical frameworks to fill this gap. This study extends a previously developed kinetic theory-based model for common-anion molten salt mixtures to reciprocal molten salt mixtures (for example, LiF–KCl) as a function of temperature and composition. To account for the effects of first nearest neighbor short-range ordering between cations and anions, pair fractions in the Modified Quasi-chemical Model in the Quadruplet Approximation were employed. The current model fills an important gap in the modeling of thermal conductivity for reciprocal molten salt mixtures, since no existing model has accurately characterized their thermal conductivity. Predicted results were compared with various equilibrium molecular dynamics simulations performed in this work for solutions involving Li^+ , Na^+ , K^+/F^- , Cl^- , as well as with existing experimental measurements. The model also predicted the thermal conductivity of reciprocal molten salt mixtures proposed in the literature as potential phase change materials. The current model demonstrated excellent predictive capability and accuracy of thermal conductivity for both monoatomic and polyatomic anion reciprocal molten salt mixtures, with an estimated error margin up to 20%. This advancement will significantly contribute to improving the statement of knowledge of reciprocal molten salt thermal conductivity and provide valuable tools for evaluating the thermal conductivity of molten salt mixtures in engineering applications.

1. Introduction

The goal of achieving carbon neutrality was established before 2050 for most countries by the Paris Agreement [1]. Renewable energy and nuclear energy are two primary sources to decarbonizing the electric power sector. Molten salt reactor is one of the Generation IV advanced nuclear reactors, in which molten salt serves as the primary nuclear coolant and/or fuel materials. However, more recently, the wind, photovoltaic and molten salt power tower multisource renewable energy cogeneration systems have become very popular to combat CO_2 emissions. Molten salts have been extensively used in metal production for over a century. For example, the Hall–Héroult process for aluminum production utilizes molten cryolite (Na_3AlF_6) as an electrolyte [2]. Similarly, metals such as titanium (Ti), zirconium (Zr), and magnesium (Mg) are produced using eutectic mixtures of NaCl–KCl as the electrolyte in their respective electrolysis processes [3]. Despite the wide

applications of molten salts in industry, some of the properties still remains not well understood, in particular the thermal conductivity. The thermal conductivity of molten salts plays a critical role in the efficiency of heat transfer in fluid mechanics. For instance, the Prandtl number, defined as $Pr = \mu C_p / \lambda$ quantifies the efficiency of heat transfer within a fluid, while the Nusselt number ($Nu = hD / \lambda$) offers key insight into the relative performance of convective versus conductive heat transfer. High thermal conductivity ensures uniform temperature distribution, preventing hot spots and overheating. As a result, the system could remain safe and efficient. Over the past several decades, the thermal conductivity of molten salts has been studied through experimental techniques, numerical simulations, and modeling. Measuring thermal conductivity through experiments is difficult and costly. Major challenges arise in accurately estimating heat losses through

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Nomenclature

Symbols

Δg	Gibbs energy
N_A	Avogadro number [mol^{-1}]
ρ	density [kg.m^{-3}]
C_p	specific heat capacity at constant pressure [$\text{kJ.mol}^{-1}\text{K}^{-1}$]
c_s	sound velocity [m.s^{-1}]
C_v	specific heat capacity at constant volume [$\text{kJ.mol}^{-1}\text{K}^{-1}$]
k_B	Boltzmann constant [J.K^{-1}]
M	molecular weight [kg.mol^{-1}]
n_s^-	total number of anionic atoms per molecule
n_s^+	total number of cationic atoms per molecule
n_a	number of atoms per molecule
n_d	number density per atom [atom.m^{-3}]
T	temperature [K]
K	complexity of local structure (dimensionless)
N	number of components in a mixture
q	absolute ionic charge
X	fraction (mole or weight depends in the text)
Y	equivalent ionic site fraction

Greek symbols

α	thermal expansivity [K^{-1}]
β_T	isothermal bulk modulus [Pa]
χ	isothermal compressibility [Pa^{-1}]
γ	Grüneisen parameter (dimensionless)
λ	thermal conductivity [$\text{W.m}^{-1}\text{K}^{-1}$]

Super/Subscripts

A	anion
C	cation
C/A	FNN pair
cal	calibrated
EX	exchange
Exp	experimental
i	index of component
id	ideal
k	kinetic
m	melting
Quad	quadruplet
Temkin	Temkin model

convection, conduction, and radiation at high temperatures. Errors caused by chemical reactions further contribute to the uncertainties [4–6]. Therefore, experimental datasets often appear scattered, inconsistent, and in disagreement regarding temperature dependence. For instance, the eutectic molten fluoride salt mixture — FLiNaK ($(\text{LiF})_{0.465}-(\text{NaF})_{0.115}-(\text{KF})_{0.42}$), which is of important interest for nuclear reactors, the discrepancy in experimental datasets is as high as 500% at around 900 [K] from individual studies [7]. Moreover, extensive experimental measurements have been carried out to determine the thermal conductivity of pure molten salts. However, molten salt mixtures are more of interest in practical engineering due to the enhanced properties.

Experimental datasets for molten salt mixtures are unfortunately quite limited, particularly for reciprocal molten salt mixtures that contain more than one cation and more than one anion. For instance, molten LiF–KCl solutions involve two cations Li^+ and K^+ , and two anions, F^- and Cl^- .

Molecular dynamics (MD) simulations offer a cost-effective way to estimate the thermal conductivity of pure and mixed molten salts. This technique also eliminates hazards linked to high-temperature measurements. However, several challenges persist, including the need for the accurate interatomic potentials and the significant computational resources required for high-order salt mixtures. Additionally, simulations can only be performed for one specific composition at a specific temperature in each run, making it time-consuming and really challenging to explore variations in composition and temperature, which are common in simulations of practical engineering processes. Despite these challenges, MD simulations can help to understand the mixing behavior and assist in validating developing models, which is the case in the present work.

Several studies have reviewed different categories of available models to predict thermal conductivity [6,8–10]. Most of these models provide relatively accurate predictions of thermal conductivity for unary molten salt. To date, the commonly employed to estimate the thermal conductivity of molten salt mixtures is the ideal mixing rule, $\lambda^{id} = \sum_{i=1}^N X_i \lambda_i$, which provided relatively good results for some salts, such as nitrate salt mixtures [9]. This model is convenient to use, only the mole fraction (X_i) and the thermal conductivity of pure molten salt (λ_i) are required of each component (i), but the reliability should be verified due to the limited availability of thermal conductivity datasets for molten salt mixtures in the literature. Additionally, it is not based on thermodynamic theory [11]. Smirnov et al. [12] proposed a model that the thermal conductivity of molten salt mixtures of common anion is inversely proportional to their molar volume. However, the experimental measurements from the study are not recommended, as they exhibited a strong positive temperature dependence on thermal conductivity, likely resulting from the improper design of the apparatus of heat losses through convection, conduction and radiation [4]. Zhao et al. [10] presented a model based on theoretical unit cell for binary mixtures, the predicted results have been compared to some experimental datasets which were not recommended, making it challenging to verify the reliability. Gheribi and Chartrand [13] developed a theoretical model based on earlier work on classical kinetic theory. The model was validated by Equilibrium MD (EMD) simulations, which showed good agreement for ternary salt LiF–NaF–KF and LiCl–NaCl–KCl common-anion mixtures. However, a “universal” constant was assumed to be effective for all ionic mixtures, which restricted the model’s wide application in different molten salt mixtures. This is especially true for molten salt mixture with large differences in the molar mass of ions and common-ion complex salt mixtures, such as LiF–CsF and LiF–BeF₂ respectively. Most of these models are tailored to a specific salt family and their mixtures. These models showed to be able to predict some of the salt mixtures with common-anion mixtures, but their reliability still needs to be questioned for applying to other salt mixtures. To the best of our knowledge, no existing model can accurately predict the thermal conductivity across a wide range of molten salt mixtures. Indeed, there is currently no model of thermal conductivity available for reciprocal molten salt mixtures.

To better illustrate reciprocal system and reciprocal solutions, Fig. 1 presents the composition of the LiF–LiCl–KF–KCl reciprocal mixture, typically plotted on a square. The pure salts are found at the four corners of the neutral plane of the four elements (Li–K–F–Cl). The four sides represent compositions in binary common-cation (LiF–LiCl, KF–KCl) and common-anion (LiF–KF, LiCl–KCl) mixtures. Within the square, four ions (Li^+ , K^+ , F^- and Cl^-) are all involved as reciprocal solutions. There is an infinite number of combinations of three or four of the four pure salts that can reproduce a given composition inside the reciprocal square (except on the sides where there is only one

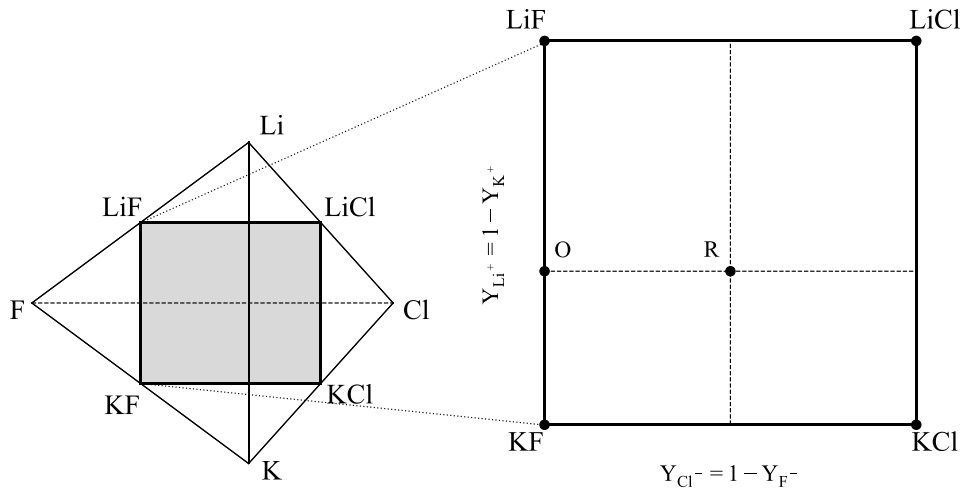


Fig. 1. Neutral plane representation of Li, K, F, and Cl, along with the composition square for the Li^+ , K^+ / F^- , Cl^- reciprocal solution. Point R illustrates an example of a reciprocal composition defined by the cationic and anionic fractions. Point O represents a common-anion mixture of $(\text{LiF})_{0.4}(\text{KF})_{0.6}$.

combination that defines the composition, this renders the previously mentioned ideal mixing rule questionable). To predict the thermal conductivity of a specific reciprocal mixture, the cationic fractions (X_C) and anionic fractions (X_A) should be defined, where C and A denote the cation and anion, respectively. By accounting the ionic charges, the equivalent site fractions (Y_C and Y_A) can be also determined, as be discussed in the next section. Therefore, the pair fractions ($X_{C/A}$) that involve the interactions of the first-nearest-neighbor (FNN) in the solution of Li^+ , K^+ , F^- and Cl^- , are defined as the ratio of the number of moles of (Li^+/F^- , Li^+/Cl^- and K^+/F^- , K^+/Cl^-) pairs to the total number of moles [14].

Let us consider an example of two monovalent reciprocal mixtures with the following nominal mole fractions: $(\text{LiF})_{0.4}(\text{KF})_{0.1}(\text{KCl})_{0.5}$ and $(\text{LiCl})_{0.4}(\text{KF})_{0.5}(\text{KCl})_{0.1}$. Using the ideal mixing rule model, thermal conductivity values of these two mixtures at 1300 [K] are calculated to be 0.727 [$\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$] and 0.538 [$\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$], respectively, with a deviation of 35.13%. However, both mixtures have the same ionic fractions at point R in Fig. 1, specifically $Y_{\text{Li}^+} = 0.4$, $Y_{\text{K}^+} = 0.6$, and $Y_{\text{F}^-} = 0.5$, $Y_{\text{Cl}^-} = 0.5$, the exchange reaction $\text{LiCl}_{\text{liq}} + \text{KF}_{\text{liq}} \rightleftharpoons \text{LiF}_{\text{liq}} + \text{KCl}_{\text{liq}}$ associated to $\Delta G_{\text{Li,K/F,Cl}}^{0,\text{EX}}$ should proceed to equilibrium at constant n_{Li^+} , n_{K^+} , n_{F^-} and n_{Cl^-} , temperature and pressure, providing a unique internal FNN pair fractions composition from the multitudes of input combinations of the four salts that give the same sets of n_{Li^+} , n_{K^+} , n_{F^-} and n_{Cl^-} . Consequently, their thermal conductivity should be only one value at this composition. This discrepancy highlights a fundamental issue with using nominal mole fractions for reciprocal molten salt mixtures (within the composition square) when applying the ideal mixing rule. Multiple combinations of nominal mole fractions can lead to identical ionic fractions, yet yield different thermal conductivity values. A same problem arises when directly applying nominal mole fractions to our previous thermal conductivity model for common-anion molten salt mixtures into reciprocal salt mixtures. Within the composition square, a specific point can represent an infinite number of nominal mole fraction combinations, resulting in an infinite number of predicted thermal conductivity values. In contrast, at the sides of the composition square, only a single composition is uniquely defined. This indicates that nominal mole fractions are well-suited for describing common-ion mixtures only, but not for reciprocal molten salt mixtures. For instance, at point O, the nominal composition of the common-anion mixture is $(\text{LiF})_{0.4}(\text{KF})_{0.6}$, with ionic fractions $Y_{\text{Li}^+} = 0.4$, $Y_{\text{K}^+} = 0.6$, and $Y_{\text{F}^-} = 1$. Using Eq. (4), the pair fractions are calculated as $X_{\text{Li}^+/\text{F}^-} = Y_{\text{Li}^+} \cdot Y_{\text{F}^-} = 0.4$, and $X_{\text{K}^+/\text{F}^-} = Y_{\text{K}^+} \cdot Y_{\text{F}^-} = 0.6$. These pair fractions are identical to the nominal mole fractions of the common-anion salt mixture.

The aim of this study is to address the existing gap by extending our previous work on thermal conductivity model for common-anion

molten salt mixtures to reciprocal molten salt solutions. In this extension, the use of nominal mole fractions for each component in reciprocal molten salt mixtures is no longer feasible. Instead, pair fractions, which account for the interactions between first nearest neighbors (FNN) of different cations and anions, are considered. The first approach, the Temkin model, assumes random mixing of cations and anions within their respective sublattices, providing one set of FNN pair fraction from a unique set of equivalent ionic fraction. However, results from the EMD simulations in this work reveal deviations from random mixing, highlighting the effects of FNN short-range ordering interactions. The second approach is the Modified Quasi-chemical Model in the Quadruplet Approximation (MQMQA) [15], in which the Gibbs energy minimization is performed with the EQUILIB Module of FactSage™ [16], finds the set of FNN pair fractions from a unique set of equilibrium ionic fractions at a fixed temperature. It evaluates combined FNN and second nearest neighbor (SNN) short-range orders. In the ideal case where $\Delta G^{EX} = 0$, the MQMQA approach reduces to the Temkin model when all common-ion interactions are ideal. Furthermore, in common-anion mixtures, the pair fractions predicted by the MQMQA approach are identical to the nominal mole fractions. Additionally, the MQMQA approach has been extensively used to derive model parameters for the thermodynamics and phase diagrams of various molten salt systems, including both common-ion and reciprocal molten salts [17–20]. A detailed discussion of the pair fractions in the Temkin model and the MQMQA approach is presented in the next section.

The MQMQA model was specifically developed to estimate pair fractions, with numerous parameters obtained and many molten salt mixtures optimized. Building on these advancements, we aim to modify the previous model for common-anion molten salt mixtures to account for reciprocal effects. Most parameters in the model will be adjusted to incorporate compositional variations affecting by the FNN pair fractions. Additionally, as part of this work and in the context of extending the FTSalt Database of FactSage™ from version 8.3 to 8.4, which already included different excess volume parameters, we have introduced several new parameters, such as thermal expansion and bulk modulus of pure salts, to enable the precise calculations of sound velocity for both pure molten salts and molten salt mixtures.

2. From nominal fractions to FNN pair fractions in the temkin model and MQMQA approach

It is important to clearly define the various types of fractions mentioned in this paper. In our previous work on common-anion mixtures [21], there is no constraint on the nominal mole fractions applied

in the model, since only one single combination uniquely defines a composition (representing the sides of the compositional square). However, in the case of reciprocal molten salt solutions (Li^+ , K^+ / F^- , Cl^-), where two or more different cations (Li^+ , K^+) and two and more anions (F^- , Cl^-) are forming in the melt (inside the compositional square), understanding the concept of FNN pair fractions becomes essential. Let us again see the example mentioned above $(\text{LiF})_{0.4}\text{-(KF)}_{0.1}\text{-(KCl)}_{0.5}$.

- Nominal fraction (X_i [mol/mol]): This refers to the initial mole fraction of each component in the melt, representing the starting proportions of each ionic species before any interactions are considered, like input moles in an experiment. In the example mixture above, $X_{\text{LiF}} = 0.4$, $X_{\text{KF}} = 0.1$, and $X_{\text{KCl}} = 0.5$.
- Cationic and anionic site (or mole) fractions (X_C and X_A): In the Temkin and quasi-chemical models, it is assumed that cations and anions reside on the cation sublattice and the anion sublattice, respectively. The cationic and anionic site fractions are defined [22]:

$$X_{C_1} = \frac{n_{C_1}}{n_{C_1} + n_{C_2}} = 1 - X_{C_2},$$

$$X_{A_1} = \frac{n_{A_1}}{n_{A_1} + n_{A_2}} = 1 - X_{A_2}, \quad (1)$$

where n_i is the number of moles of ion i in the solution. In the example, we have $X_{\text{Li}^+} = 0.4/(0.4 + 0.5 + 0.1) = 0.4$, $X_{\text{K}^+} = 0.6$, $X_{\text{F}^-} = (0.4 + 0.1)/(0.4 + 0.1 + 0.5) = 0.5$, and $X_{\text{Cl}^-} = 0.5$.

- Equivalent site fractions (Y_C and Y_A): These fractions account for ionic charges ($|q_i|$) to ensure an equal number of equivalents on each sublattice. For instance, in pure CaCl_2 , $q_{\text{Ca}^{2+}} = 2q_{\text{Cl}^-}$. The equivalent cationic and anionic fractions are given [23]:

$$Y_{C_1} = \frac{q_{C_1} * n_{C_1}}{q_{C_1} * n_{C_1} + q_{C_2} * n_{C_2}} = 1 - Y_{C_2}, \quad (2)$$

$$Y_{A_1} = \frac{q_{A_1} * n_{A_1}}{q_{A_1} * n_{A_1} + q_{A_2} * n_{A_2}} = 1 - Y_{A_2}, \quad (3)$$

this is a monovalent reciprocal mixture, we have $|q_i| = 1$ for all ions. Therefore, $Y_{\text{Li}^+} = 0.4$, $Y_{\text{K}^+} = 0.6$, $Y_{\text{F}^-} = 0.5$, and $Y_{\text{Cl}^-} = 0.5$.

- Pair fractions of FNN in the Temkin model ($X_{C/A}^{\text{Temkin}}$): The Temkin model assumed random mixing of cations on cationic sites and anions on anionic sites. Therefore, the FNN pair fractions can be estimated based on the random mixing between cations and anions. The following equation gives the probability of the FNN pair in the Temkin model,

$$X_{C/A} = Y_C * Y_A \quad (4)$$

Consequently, the pair fractions for each component in the Temkin model are given as: $X_{\text{LiF}}^{\text{Temkin}} = Y_{\text{Li}^+} * Y_{\text{F}^-} = 0.4 * 0.5 = 0.2$, $X_{\text{LiCl}}^{\text{Temkin}} = Y_{\text{Li}^+} * Y_{\text{Cl}^-} = 0.2$, and $X_{\text{KF}}^{\text{Temkin}} = Y_{\text{K}^+} * Y_{\text{F}^-} = 0.6 * 0.5 = 0.3$, $X_{\text{KCl}}^{\text{Temkin}} = Y_{\text{K}^+} * Y_{\text{Cl}^-} = 0.3$, these values are independent of temperature in Temkin model.

- Pair fractions in the MQMQA approach ($X_{C/A}^{\text{MQMQA}}$) [15]: The MQMQA uses an internal composition of quadruplets, formed by two cations and two anions, to reproduce the Gibbs energy of a multi-component solution. Each quadruplet has a Gibbs energy function, the equilibrium quadruplet composition is obtained by minimizing the Gibbs energy at constant temperature and pressure, and moles of ions. From the equilibrium quadruplet fractions, FNN pair fractions can be computed. The expression for the pair fraction in the MQMQA ($X_{C/A}^{\text{MQMQA}}$) is shown:

$$X_{C/A}^{\text{MQMQA}} = X_{(C_1)_2/(A_1)_2}^{\text{Quad}} + \frac{1}{2} X_{C_1 C_2/(A_1)_2}^{\text{Quad}} + \frac{1}{2} X_{(C_1)_2/A_1 A_2}^{\text{Quad}} + \frac{1}{4} X_{C_1 C_2/A_1 A_2}^{\text{Quad}} + \dots \quad (5)$$

where $X_{C_1 C_2/A_1 A_2}^{\text{Quad}}$ are the quadruplet fractions.

For a detailed explanation of “quadruplets”, please refer to the works of Pelton et al. [15,22,23].

Table 1

Calculated equilibrium pair fractions in the MQMQA approach for the nominal fraction of $(\text{LiF})_{0.4}\text{-(KF)}_{0.1}\text{-(KCl)}_{0.5}$ molten salt mixture as a function of temperature, starting from the liquidus temperature (around 950 [K]), compared to the pair fractions in the Temkin model.

$X_{C/A}^{\text{MQMQA}} \setminus T$ [K]	950	1150	1350	1550	$X_{C/A}^{\text{Temkin}}$ (all T)
$X_{\text{LiF}}^{\text{MQMQA}}$	0.2896	0.2742	0.2633	0.2554	0.2
$X_{\text{LiCl}}^{\text{MQMQA}}$	0.1157	0.1312	0.1420	0.1499	0.2
$X_{\text{KF}}^{\text{MQMQA}}$	0.2104	0.2258	0.2367	0.2446	0.3
$X_{\text{KCl}}^{\text{MQMQA}}$	0.3843	0.3688	0.3580	0.3501	0.3

The pair fractions in the MQMQA approach and the Temkin model (temperature independent), for $(\text{LiF})_{0.4}\text{-(KF)}_{0.1}\text{-(KCl)}_{0.5}$, are presented in Table 1 as a function of temperature. The significant deviation is primarily attributed to the interaction caused by the short-range ordering in the FNN. Furthermore, as the temperature increases, the solution becomes more disordered and are more likely to reside in their respective sites in a random manner, approaching the ideal case of random mixing described by the Temkin model. Please note that if the nominal composition is $(\text{LiCl})_{0.4}\text{-(KF)}_{0.5}\text{-(KCl)}_{0.1}$ (as presented in the previous section), the ionic fraction of Li^+ , K^+ , F^- , and Cl^- in the melt will be the same with those of the example composition in the table, resulting in identical pair fractions in the MQMQA.

3. Equilibrium molecular dynamics simulations for Li^+ , Na^+ , K^+ / F^- , Cl^-

The methodology for determining thermal conductivity using equilibrium molecular dynamics (EMD) has been extensively described in previous works, along with the force field formalism used to model inter-ionic interactions. These details will not be repeated here, please refer to [21,24–27] for further information. In brief, we first carried out two series of simulations in the NPT ensemble at the target temperature of 1300 [K] to generate thermally equilibrated configurations, with the simulation time of 2 ns. Then, a new series of EMD simulations was performed in the NVT based on the thermally equilibrated configurations obtained in the NPT simulations, with simulation time of 10 ns. In both NPT and NVT simulations, the temperature was controlled by a Nosé–Hoover thermostat, and the pressure in the NPT simulations was controlled using an extension of the Martyna barostat [28]. The relaxation times for both the thermostat and barostat were set to 0.5 ps. All simulations were performed using periodic boundary conditions and the minimum image convention.

The determination of thermal conductivity is based on the GK approach, where the Onsager phenomenological coefficients are calculated via EMD (L_{nm}), and the thermal conductivity is obtained through the autocorrelation function in thermodynamic equilibrium, defined as [29]:

$$L_{mn}(\tau) = \frac{1}{3k_B V} \int_0^\tau \langle \mathbf{J}_m(t) \cdot \mathbf{J}_n(0) \rangle dt \quad (6)$$

where n , and m are indices that can that the values e and/or z_i , corresponding to the energy current and the mass current of ion i , respectively.

The standard error associated with the thermal conductivity was calculated using a block averaging method. For a detailed explanation, refer to [30]. The number of blocks, 20, was chosen in our studies to be proportional to the total simulation time and was determined following a convergence test.

Thermal conductivity is calculated from the simulated phase trajectory using the Green–Kubo formalism [31], which enables the interpretation of thermal conductivity based on energy and charge fluctuations from EMD simulations. The total NVT run was divided into 20 blocks of 0.5 ns, and the transport coefficients were computed independently for each block. In order to ensure convergence of thermal conductivity,

a correlation time (τ) of 5 ps was chosen. The thermal conductivity of a thermally equilibrated system is determined by averaging the values of all the blocks, which can be written as follows:

$$\lambda(n_{ion_i}, T) = \lim_{\tau \rightarrow \infty} \langle \lambda(\tau, T, n_{ion_i}) \rangle_{all \text{ blocks}} \quad (7)$$

To simulate the phase trajectory, the Polarizable Ion Model (PIM) force field was employed, with parameters for the Li^+ , Na^+ , K^+ / F^- , Cl^- systems determined *ab initio* molecular dynamics, based on reproducing forces and dipoles obtained through DFT calculations. Notably, the PIM force field has demonstrated high accuracy in simulating both salt families, and numerous studies have utilized it to derive thermal conductivity values with remarkable precision [13,24,32,33]. Three reciprocal mixtures have been simulated using the PIM EMD for the fluoride and chloride families. The simulated mixtures include $(\text{Li}^+, \text{Na}^+) / (\text{F}^-, \text{Cl}^-)$; $(\text{Li}^+, \text{K}^+) / (\text{F}^-, \text{Cl}^-)$; and $(\text{Na}^+, \text{K}^+) / (\text{F}^-, \text{Cl}^-)$. To generate the phase trajectory required for extracting thermal conductivity using the Green–Kubo (GK) method at 1300 [K], well above the melting point of the pure molten salt. The simulations were performed with compositions varying in increments of 0.25 mole fraction for both cations and anions. This approach ensures comprehensive coverage of the entire compositional range of the reciprocal mixtures. In each simulation, a total of 864 ions (432 cations and 432 anions) were included, with the equilibrium volume determined by a prior simulation in the isobaric–isothermal statistical ensemble (NPT) at the corresponding temperatures and a pressure of 10^5 Pa. Two sets of NPT simulations were initially performed at the designed simulating temperature. These simulations generated thermally equilibrated configurations. Following this, a new series of EMD simulations were conducted in the canonical statistical ensemble (NVT) to determine the thermal conductivity of the mixtures, using the configurations obtained from the previous NPT simulations. The volume in the NVT simulations remained fixed.

4. Model of thermal conductivity for common-anion and common-cation molten salt mixtures with pair fractions ($X_{C/A}$)

In our previous work [21], we proposed a thermal conductivity model for simple common-anion molten salt mixtures. The model showed a reduced thermal conductivity, which is attributed to the specific characteristics of the ions, such as the atomic masses, ionic sizes, and neighbor coupling forces between host and solute atoms. A mass fluctuation term (Γ) is included to account for the disorder effect within the short-range quasi-crystalline lattice of the liquid salt solutions. The formulation is given as follows [21]:

$$\lambda(\underline{X}_i, T) \approx \lambda^k(\underline{X}_i, T) \left[1 - \underbrace{\sum_{i=1}^N \left(\frac{\lambda_i^0(T)}{\lambda^{id}(T)} \right) X_i \left(1 - \frac{M_i}{\bar{M}(\underline{X}_i)} \right)^2}_{\text{Mass fluctuation } (\Gamma)} \right] \quad (8)$$

where $\underline{X}_i$, N , λ_i^0 , λ^{id} , M_i and $\bar{M}$ represent the vector of nominal mole fractions, total number of components, thermal conductivity of the i component of pure molten salt, ideal thermal conductivity (based on the ideal mixing rule), molar mass of the i component, and the molar mass of the mixture, respectively. The thermal conductivity of molten salt mixture as a function of temperature dependence without considering the mass fluctuation term is expressed:

$$\lambda^k(\underline{X}_i, T) = K(\underline{X}_i) k_B n_d^{2/3}(\underline{X}_i, \underline{T}_{m,i}) \langle c_s \rangle_{liq}(\underline{X}_i, \underline{T}_{m,i}) \left[1 - \alpha(\underline{X}_i, \underline{T}_{m,i}) \left(\gamma(\underline{X}_i, \underline{T}_{m,i}) + \frac{1}{3} \right) (T - \underline{T}_{m,i}) \right], \quad (9)$$

where k_B , n_d $liq = (n_a N_A) / V(\underline{T}_{m,i}, \underline{X}_i)$, n_a , N_A , c_s , α , and γ are the Boltzmann constant, number density of atoms, number of atoms, Avogadro number, speed of sound, thermal expansivity and the Grüneisen parameter at the melting point ($\underline{T}_{m,i}$). K is an introduced material constant to characterize the complexity of the chemical nature (local structure)

of unary molten salts, as established in our previous study [34]. It is defined as:

$$K = 1 + \frac{n_s^+}{n_s^-}, \quad (10)$$

n_s^+ and n_s^- the number of species involved in cationic and anionic ions, respectively. For example, in the case of LiF , $K = 1 + 1/1 = 2$, and for NaNO_3 $K = 1 + 1/4 = 1.25$. For the case of polymerizing molten salts such as BeF_2 , $K = 1$.

As a result, the model can be expressed in terms of pair fractions (denoted as $X_{C/A}$), leading to the following equation for common-anion mixtures:

$$\lambda(\underline{X}_{C/A}, T) \approx \lambda^k(\underline{X}_{C/A}, T) \left[1 - \sum_{C=1}^{N_C} \left(\frac{\lambda_{C/A}^0(T)}{\lambda^{id}(T)} \right) X_{C/A} \left(1 - \frac{M_{C/A}}{\bar{M}(\underline{X}_{C/A})} \right)^2 \right] \quad (11)$$

Similarly, for the case of common-cation mixtures, replace $\sum_{C=1}^{N_C}$ with $\sum_{A=1}^{N_A}$. It is important to note that in our previous work [21], we validated the predicted thermal conductivity only for common-anion molten salt mixtures.

5. Modeling the temperature and composition dependence of thermal conductivity of reciprocal molten salt mixtures with the MQMQA

The sound velocity has been first evaluated using the pure molten salt model [34] as a function of temperature, rather than using its value at the melting point. The expression gives:

$$c_s = \left(\frac{\beta_T C_p}{\rho C_v} \right)^{0.5}, \quad (12)$$

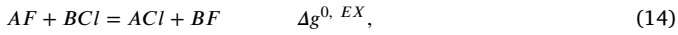
where β_T , C_p , and C_v represents the isothermal bulk modulus, the specific heat capacity at constant pressure, and the specific heat capacity at volume constant. All these values can be obtained using the EQUILIB Module of FactSage™, which determines the equilibrium values of C_p , C_v , ρ , β_T for a salt component at a given temperature and pressure through Gibbs energy minimization [16], it also calculates all equilibrium quadruplet mole fractions. From the thermodynamic and volumetric model parameters in the FTsalt Database of FactSage™, numerical derivatives can be computed mathematically with at least 6 digital precisions of these parameters based on the value of Gibbs energy. Fig. A.1 (in the Appendix) illustrates the sound velocity calculated using the latest FTsalt Database [17,35,36] of FactSage™ 8.4. The results show excellent agreement with the experimental measurements reported by Prissaijnyi et al. [37] as a function of composition at 1100 [K]. The supplementary materials demonstrate that we successfully reproduced the sound velocity of pure salts, common-ion mixtures, and reciprocal mixtures, achieving accuracy comparable to experimental measurements. Eventually, the λ^k can be simplified by using these temperature-dependent parameters, a general formulation can be written as follows:

$$\lambda^k(\underline{X}_{C/A}, T) = K(\underline{X}_{C/A}) k_B n_d^{2/3}(\underline{X}_{C/A}, T) \langle c_s \rangle_{liq}(\underline{X}_{C/A}, T) \quad (13)$$

In this general expression, the FNN pair fractions can be estimated using various methods, including EMD simulations, experimental techniques (for example, spectroscopy), and theoretical models (for example, Temkin, quasi-chemical models). The thermal conductivity values obtained from these methods differ from one another due to differences in FNN pair fractions. Compared to Eq. (9), Eq. (13) no longer requires the melting temperature of the pure salts.

As previously mentioned, nominal mole fractions cannot be directly applied to predict the thermal conductivity of reciprocal salt mixtures, where more than one cation and more than one anion are present.

Since in a reciprocal salt solution, the FNN short-range ordering interactions can be very strong between cation–anion, causing considerable deviations in the FNN pair fractions from the random mixing (Temkin model). These interactions are notably complex due to the significant impact of both FNN and second-nearest-neighbor (SNN) short-range ordering [15]. Reciprocal salt solutions of fluoride and chloride mixtures have been performed in EMD in this work, showing a clear occurrence of FNN short-range ordering. The extent of the reactions is determined by the exchange reactions of Gibbs energy ($\Delta g^{0, EX}$) [17,22]:



where A, B represent different cations.

In this paper, we extend the thermal conductivity model for common-ion mixtures to reciprocal molten salt mixtures by incorporating the FNN short-range ordering pairs within the MQMQA approach, in terms of temperature and compositional dependence. The current model can be represented using the pair fractions in the MQMQA approach ($X_{C/A}^{MQMQA}(T)$) defined in Eq. (5) as follows:

$$\begin{aligned} \lambda_{C/A}^{MQMQA}(T, T) & \approx \lambda_{C/A}^{MQMQA}(T, T) \left[1 - \sum_{C=1}^{N_C} \sum_{A=1}^{N_A} \left(\frac{\lambda_{C/A}^0(T)}{\lambda_{C/A}^{MQMQA}(T, T)} \right) \right] \\ & X_{C/A}^{MQMQA}(T) \left[1 - \frac{M_{C/A}}{M_{C/A}^{MQMQA}(T)} \right]^2, \end{aligned} \quad (15)$$

please note that the pair fractions $X_{C/A}^{MQMQA}$ are temperature dependent at a same composition. The kinetic theory based thermal conductivity of liquid salt mixtures without considering the mass fluctuation in pair fraction is expressed:

$$\lambda_{C/A}^{MQMQA}(T, T) = K(X_{C/A}^{MQMQA}(T)) k_B n_d^{2/3} (X_{C/A}^{MQMQA}(T, T) \langle c_s \rangle_{liq} (X_{C/A}^{MQMQA}(T, T))) \quad (16)$$

where $\lambda_{C/A}^0(T)$ represents the thermal conductivity of each pure component, determined using Eq. (16). $\lambda_{C/A}^{MQMQA}(T, T)$ is the thermal conductivity calculated from the pair fractions in the MQMQA approach using the ideal mixing rule with the calculated equilibrium pair fraction vector of MQMQA. In the case of simple common-ion mixtures, where the interatomic interactions are neglected, pair fractions in the MQMQA model ($X_{C_1C_2/A}^{MQMQA}$) are identical to those of nominal fractions.

6. Results and discussion

Most available experimental works found in the literature are on pure molten salts and some eutectic compositions of common-ion molten salt mixtures. These experimental datasets are scarce and show disagreement in their temperature dependence, which is attributed to differences in experimental techniques and measurement conditions. Various studies [4,6,9] emphasize that datasets exhibiting a negative temperature dependence are considered reliable. The works reported by Nagasaka et al. [8,38,39,39–45] and Harada et al. [46,47] were selected as reliable references in our previous model development. In this work, since there are few experimental measurements of thermal conductivity for reciprocal molten salt mixtures, numerous EMD simulations have been performed to validate the developed model. Very few experimental datasets on the thermal conductivity of reciprocal molten salt solutions are available in the literature. The same methodology used in our previous work was applied [21]. Initially, we calibrated the thermal conductivity of pure molten salts to match the EMD results for the pure salts of LiF, NaF, KF, LiCl, NaCl, and KCl. Subsequently, we assessed the thermal conductivity behaviors of reciprocal liquid solutions along with the compositions. Some common-cation mixtures

were simulated meanwhile using EMD, the model was further evaluated for some common-cation mixtures (available in the supplementary material) in comparison with the common-cation mixtures simulated by EMD.

The aim of this work is to model the thermal conductivity of reciprocal molten salt mixtures in considering interatomic interactions of FNN short-range ordering between different cations and anions within melt. The predictions of the current model showed less than 20% error compared to EMD simulation results for the three reciprocal mixtures of fluoride and chloride, which demonstrated higher accuracy than the ideal mixing rule (λ^{id}). Moreover, the predictions are assessed by comparing it to available experimental data in the literature for the HITEC salt and the mixture of NaF–NaCl–KCl for solar energy application. Finally, the current model's predictive capability is further demonstrated by its capability to estimate the thermal conductivity of reciprocal molten salt PCMs, which were proposed for energy storage applications, accounting both for temperature and compositional dependence. It is expected that the current model also validates for the molten mixtures of polyatomic salt mixtures, such as nitrates, carbonates. Overall, the current model provides significant benefit in the estimation for the efficient assessment of thermal conductivity. Its potential applications include serving as a valuable reference for molten salt databases and helping to as a powerful tool for molten salt materials evaluations across diverse compositions and temperatures in industrial settings.

6.1. Model evaluation and validation using EMD results and experiential data

6.1.1. (Li^+ , Na^+ , K^+) / (F^- , Cl^-) reciprocal solutions

EMD simulations for three reciprocal molten salt solutions including (Li^+ , Na^+) / (F^- , Cl^-), (Li^+ , K^+) / (F^- , Cl^-), and (Na^+ , K^+) / (F^- , Cl^-) have been performed with an increment of 0.25 mole fraction of cation and anion at 1300 [K]. The EMD results have the error range of $\pm 15\%$ – 30% . To provide a clear representation of the data's accuracy, a 20% error margin was applied to each EMD result for visualization purposes. The cations (Li^+ , Na^+ , K^+) and anions (F^- , Cl^-) will exchange in between, and form LiF, LiCl, NaF, NaCl, KF, and KCl with different pair fractions. The Gibbs energy of exchange, $\Delta g_{C_1C_2/FCI}^{EX}$ has a strong impact on the equilibrium pair fractions. For example, in the case of LiF–KCl, $\text{LiF} + \text{KCl} \rightleftharpoons \text{LiCl} + \text{KF}$, $|\Delta g_{C_1C_2/FCI}^{EX}| = 57.4$ [kJ/mol] at 1300 [K], LiF and KCl pairs predominate in the melt.

a. (Li^+ , Na^+) / (F^- , Cl^-) reciprocal mixture

Fig. 2 presents the predicted thermal conductivities for the LiF–NaCl and NaF–LiCl mixtures as a function of composition. The red dashed line corresponds to predictions based on end-member parameters calibrated (λ_{cal}) to the EMD results instead of our assessed values [34]. This calibration approach provides insights into the behaviors of compositional dependence of reciprocal molten salt solutions. As shown in the sub-figures, the predictions from the present model exhibit high accuracy, closely matching the compositional trends and predicted values within a margin of 20%. The black solid line represents the model's predictions, which align well with reliable experimental datasets for the end members. Although no experimental data are currently available in the literature for the reciprocal mixture (Li^+ , Na^+ / F^- , Cl^-), we are confident with reliability of the model's predictions (black solid line) with an accuracy of approximately 20%. At the nominal composition $X_{nominal} = 0.5$, the predicted thermal conductivity is identical for both molten reciprocal LiF–NaCl and NaF–LiCl mixtures, with $\lambda_{C/A}^{MQMQA} = 0.5501$ [W·m⁻¹·K⁻¹], since their pair fractions are identical. In addition, both mixtures exhibit significant deviations from ideal mixing calculations. The LiF–NaCl mixture, in particular, exceeds the predicted thermal conductivity value by 57%. These deviations are attributed to the large differences in molar masses and thermal conductivities between the pure salts, which contribute to the observed discrepancies.

Table 2 presents the comparison between the ionic fractions, the pair fractions calculated by the Temkin model, and those calculated

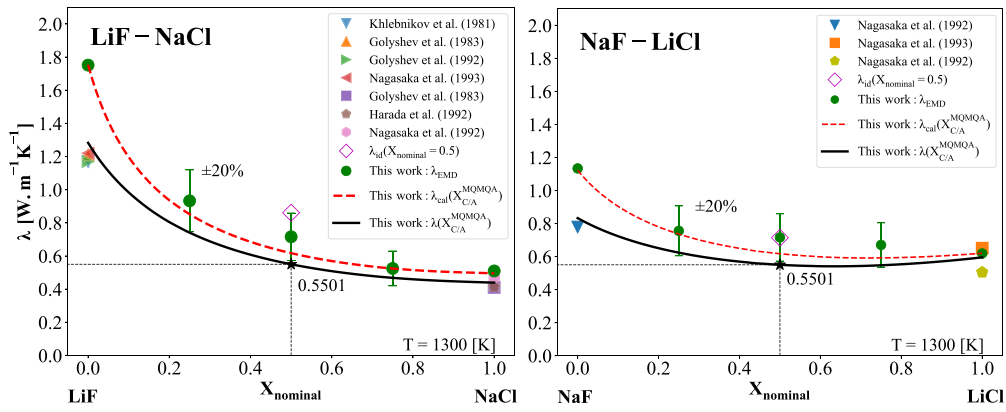


Fig. 2. Predicted thermal conductivity values of reciprocal Li^+ , Na^+ / F^- , Cl^- molten salt mixtures in comparison to EMD results and to recommended experimental results at 1300 [K] reported by Khlebnikov et al. [48], Golyshev et al. [49,50], Nagasaka et al. [8,51], Harada et al. [46]. At the nominal composition $X_{\text{nominal}} = 0.5$, both reciprocal mixtures have an identical thermal conductivity of $\lambda_{\text{LiNa/FCl}}^{\text{MQMQA}} = 0.5501$ [$\text{W.m}^{-1}\text{K}^{-1}$].

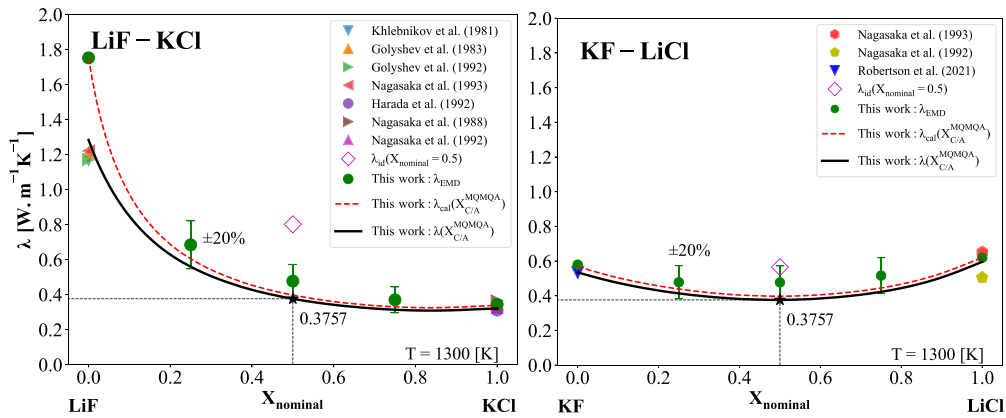


Fig. 3. Predicted thermal conductivity values of reciprocal (Li^+ , K^+ / F^- , Cl^-) molten salt mixture in comparison to EMD results and to recommended experimental results at 1300 [K] reported by Khlebnikov et al. [48], Golyshev et al. [49,50], Nagasaka et al. [8,39,51], Harada et al. [46], Robertson et al. [52]. At the nominal composition $X_{\text{nominal}} = 0.5$, both reciprocal mixtures have an identical thermal conductivity of $\lambda_{\text{LiK/FCl}}^{\text{MQMQA}} = 0.3757$ [$\text{W.m}^{-1}\text{K}^{-1}$].

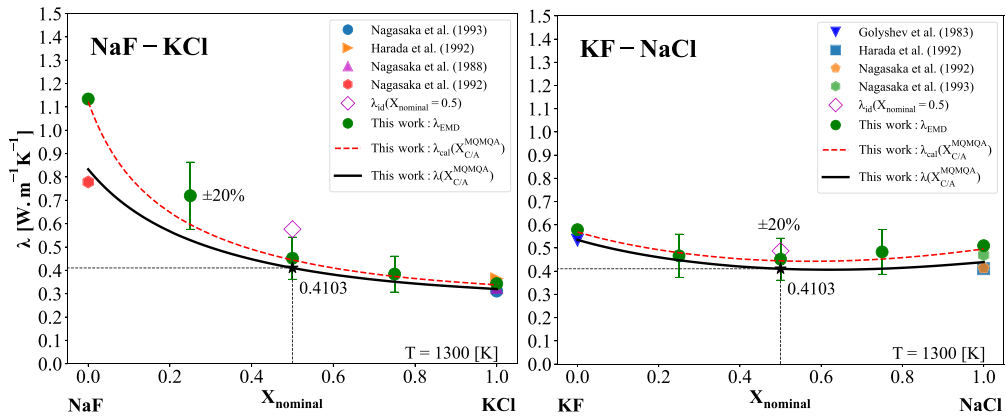


Fig. 4. Predicted values of reciprocal Na^+ , K^+ / F^- , Cl^- mixtures in comparison to MD results and two end member of reliable experimental results at 1300 [K] reported by Nagasaka et al. [8,39,51], Golyshev et al. [49], Harada et al. [46]. At the nominal composition $X_{\text{nominal}} = 0.5$, both reciprocal mixtures have an identical thermal conductivity of $\lambda_{\text{NaK/FCl}}^{\text{MQMQA}} = 0.4103$ [$\text{W.m}^{-1}\text{K}^{-1}$].

using the MQMQA approach. The results reveal notable differences between random mixing and the pair fractions in the FNN short-range ordering of MQMQA approach. These deviations arise from the contribution of interatomic exchange of the Gibbs energy (Δg^{EX}). The magnitude of $|\Delta g^{\text{EX}}|$, determines the extent of deviation from the random mixing (Temkin model). For instance, at a nominal composition of $(\text{LiF})_{0.5} - (\text{NaCl})_{0.5}$, the random mixing assumption predicts equal

contributions of 0.25 [mol/mol] for each pure component. However, with $|\Delta g_{\text{LiNa/FCl}}^{\text{EX}}| = 35.4$ [kJ/mol] at 1300 [K] (Calculated by FactSage™), LiF and NaCl dominate in the melt, $X_{\text{LiF}}^{\text{MQMQA}} = 0.2889$ and $X_{\text{NaCl}}^{\text{MQMQA}} = 0.2889$. It is observed that the fractional difference (y) remains consistent across the components, reflecting an increase of probability of FNN cation-anion pairs from random mixing (Temkin model $X_{\text{C/A}}^{\text{Temkin}} = Y_{\text{C}} * Y_{\text{A}}$) to non-random mixing (MQMQA). For

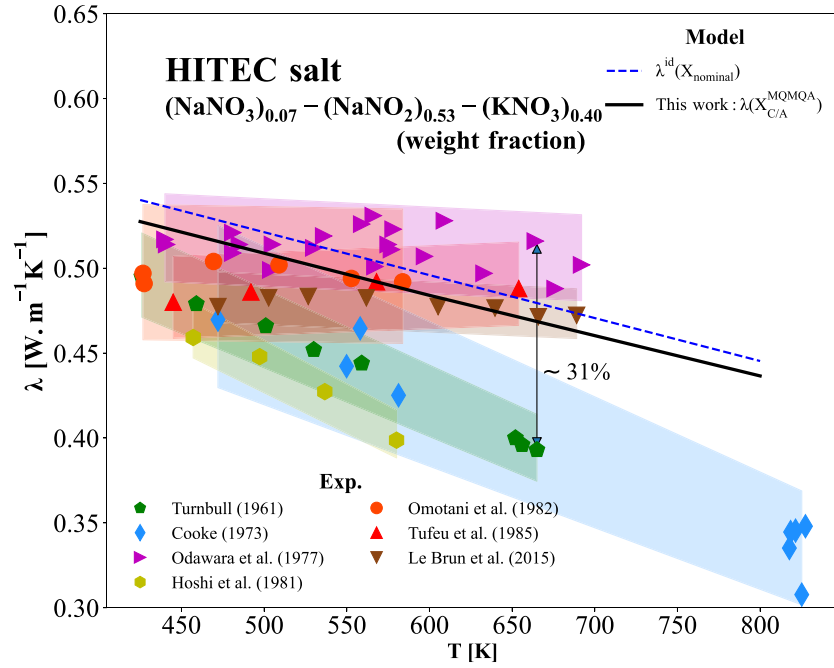


Fig. 5. Predicted thermal conductivity values of HITEC salt mixture $(\text{NaNO}_3)_{0.07}-(\text{NaNO}_2)_{0.53}-(\text{KNO}_3)_{0.40}$ weight fraction, corresponding to approximately 0.066:0.616:0.318 in mole fraction) in comparison to the recommended experimental datasets reported by Turnbull [53], Cooke [54], Odawara et al. [55], Hoshi et al. [56], Omotani et al. [57], Tufeu et al. [58] and Le Brun et al. [59], as a function of temperature.

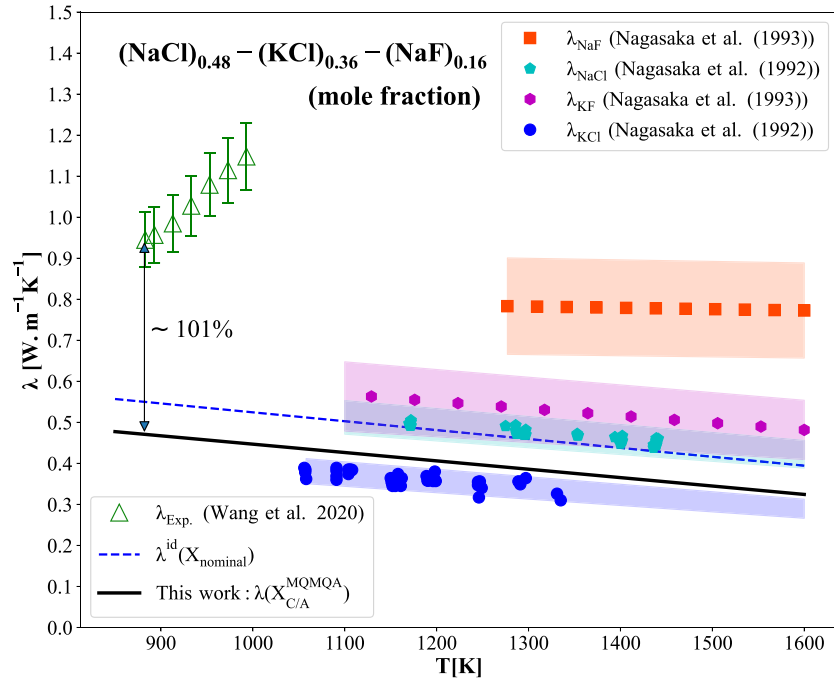


Fig. 6. Predicted thermal conductivity values for the ternary salt $(\text{NaCl})_{0.48}-(\text{KCl})_{0.36}-(\text{NaF})_{0.16}$ (mole fraction) molten mixture compared with recommended experimental data four pure salts reported by Nagasaka et al. [8,51] as a function of temperature.

instance, as demonstrated in the example above, the relationships are $X_{\text{LiF}} = Y_{\text{Li}^+} * Y_{\text{F}^-} + y$, $X_{\text{NaCl}} = Y_{\text{Na}^+} * Y_{\text{Cl}^-} + y$, $X_{\text{NaF}} = Y_{\text{Na}^+} * Y_{\text{F}^-} - y$, and $X_{\text{LiCl}} = Y_{\text{Li}^+} * Y_{\text{Cl}^-} - y$ [22,88], where the largest difference between two approaches is shown by $|y| = 0.0389$. Thus, the MQMQA approach offers a more accurate representation of molten salt behavior compared to the random mixing assumption by considering the effects of FNN and SNN short-range ordering interactions and $|Ag_{\text{LiNa/FCI}}^{EX}|$.

b. $(\text{Li}^+, \text{K}^+) / (\text{F}^-, \text{Cl}^-)$ reciprocal mixture

Fig. 3 compares the EMD simulation results with the calibrated predictions (red dashed line) for the reciprocal mixtures LiF–KCl and KF–LiCl, alongside the predictions of the present model (black solid line). The predictions from the current model align well with the EMD results, both in terms of compositional trends and thermal conductivity values, with deviations within a 20% error margin. At $X_{\text{nominal}} = 0.5$, both mixtures have a same thermal conductivity value of $0.3757 \text{ [W.m}^{-1}\text{K}^{-1}]$. In the reciprocal mixture of LiF–KCl, the estimated thermal conductivity value based on the ideal mixing rule is approximately

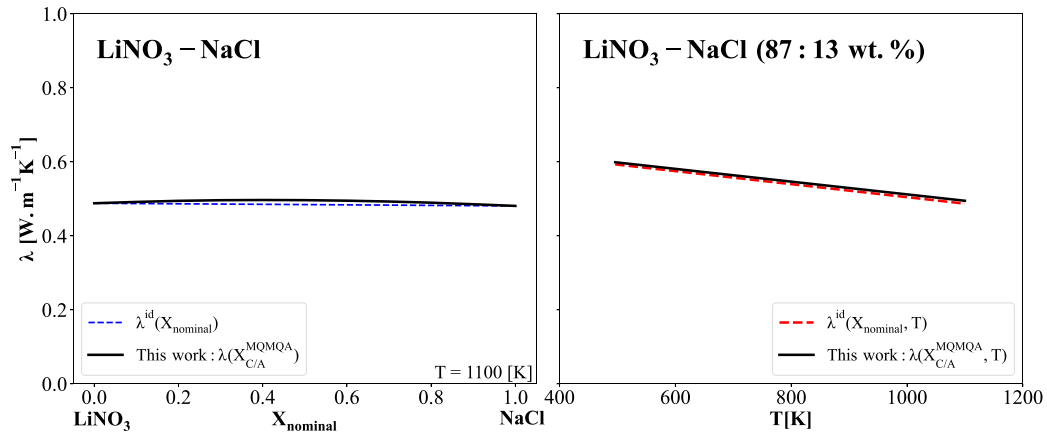


Fig. 7. Predicted thermal conductivity values for reciprocal LiNO₃-NaCl molten mixture as a function of composition at 1100 [K] and temperature dependence for the designed composition of 87:13 wt.% or 0.85:0.15 in mole fraction.

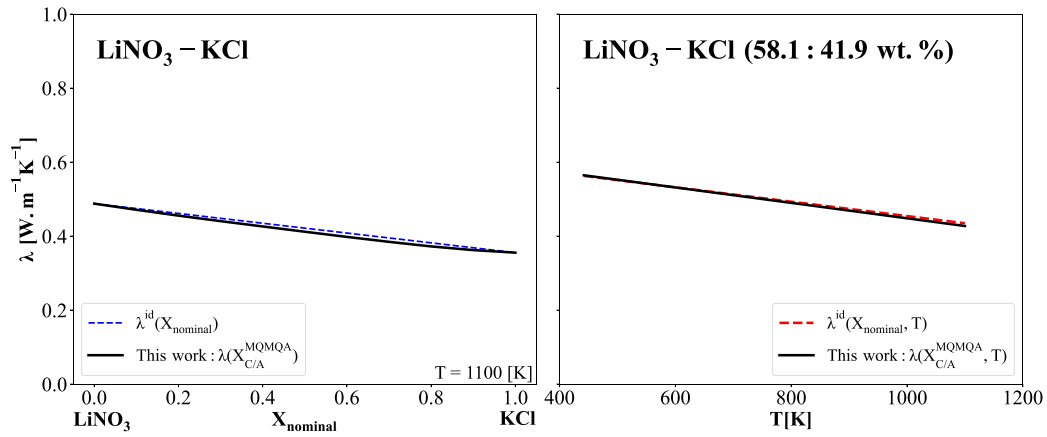


Fig. 8. Predicted thermal conductivity values for reciprocal LiNO₃-KCl molten mixture as a function of composition at 1100 [K] and temperature dependence for the designed composition of 58.1:41.9 wt.% or 0.6:0.4 in mole fraction.

Table 2

Comparison of different ionic fractions of Li⁺, Na⁺/F⁻, Cl⁻ with their corresponding random mixing fractions and pair fractions estimated by the MQMQA approach at 1300 [K].

Cationic and anionic fractions	Fractions	LiF	NaF	LiCl	NaCl
0.75 Li ⁺ , 0.25 Na ⁺ /0.75 F ⁻ , 0.25 Cl ⁻	Random mixing (Temkin)	0.5625	0.1875	0.1875	0.0625
	FNN per MQMQA	0.5836	0.1664	0.1664	0.0836
	Difference (y)	0.0211	0.0211	0.0211	0.0211
0.75 Li ⁺ , 0.25 Na ⁺ /0.25 F ⁻ , 0.75 Cl ⁻	Random mixing (Temkin)	0.1875	0.5625	0.0625	0.1875
	FNN per MQMQA	0.2099	0.5401	0.0401	0.2099
	Difference (y)	0.0224	0.0224	0.0224	0.0224
0.5 Li ⁺ , 0.5 Na ⁺ /0.5 F ⁻ , 0.5 Cl ⁻	Random mixing (Temkin)	0.25	0.25	0.25	0.25
	FNN per MQMQA	0.2889	0.2111	0.2111	0.2889
	Difference (y)	0.0389	0.0389	0.0389	0.0389
0.25 Li ⁺ , 0.75 Na ⁺ /0.75 F ⁻ , 0.25 Cl ⁻	Random mixing (Temkin)	0.1875	0.0625	0.5625	0.1875
	FNN per MQMQA	0.2086	0.0414	0.5414	0.2086
	Difference (y)	0.0211	0.0211	0.0211	0.0211
0.25 Li ⁺ , 0.75 Na ⁺ /0.25 F ⁻ , 0.75 Cl ⁻	Random mixing (Temkin)	0.0625	0.1875	0.1875	0.5625
	FNN per MQMQA	0.0874	0.1626	0.1626	0.5874
	Difference (y)	0.0249	0.0249	0.0249	0.0249

0.8 [W.m⁻¹.K⁻¹], which shows a significant large deviation at $X_{\text{nominal}} = 0.5$, exceeding 110%. This discrepancy arises from the substantial differences in molar masses and thermal conductivities of the end members (LiF and KCl), as well as the very important Gibbs energy of exchange within the solution. For both the LiF-KCl and KF-LiCl mixtures, the model predictions are slightly smaller than the EMD results. This dependency can be explained by two factors: 1. The EMD simulations employed the PIM method, which tends to overestimate thermal

conductivity for LiF by about 38% compared to the recommended experimental data, as the non-polarizable nature of LiF. The small Li⁺/F⁻ pair fractions in the melt may slightly increase the EMD results of the reciprocal melts. 2. The exchange of different cations and anions in the solution forms new salts, which likely helps stabilize the overall solution by reducing the mass fluctuations. For example, two new salts, LiCl and KF, are formed in the solution within the LiF-KCl melt. The overestimated LiF contributions in the EMD results may

Table 3

Comparison of different ionic fractions of Li^+ , K^+/F^- , Cl^- with their corresponding random mixing fractions and pair fractions estimated by the MQMQA approach at 1300 [K].

Cationic and anionic fractions	Fractions	LiF	KF	LiCl	KCl
0.75 Li^+ , 0.25 K^+/F^- , 0.25 Cl^-	FNN per MQMQA	0.5868	0.1536	0.1536	0.1060
0.75 Li^+ , 0.25 K^+/F^- , 0.75 Cl^-	FNN per MQMQA	0.2232	0.5208	0.0329	0.2232
0.5 Li^+ , 0.5 K^+/F^- , 0.5 Cl^-	Random mixing (Temkin)	0.25	0.25	0.25	0.25
	FNN per MQMQA	0.3140	0.1860	0.1860	0.3140
	Difference ($ y $)	0.064	0.064	0.064	0.064
0.25 Li^+ , 0.75 K^+/F^- , 0.25 Cl^-	FNN per MQMQA	0.2245	0.0313	0.5196	0.2245
0.25 Li^+ , 0.75 K^+/F^- , 0.75 Cl^-	FNN per MQMQA	0.1122	0.1479	0.1479	0.5920

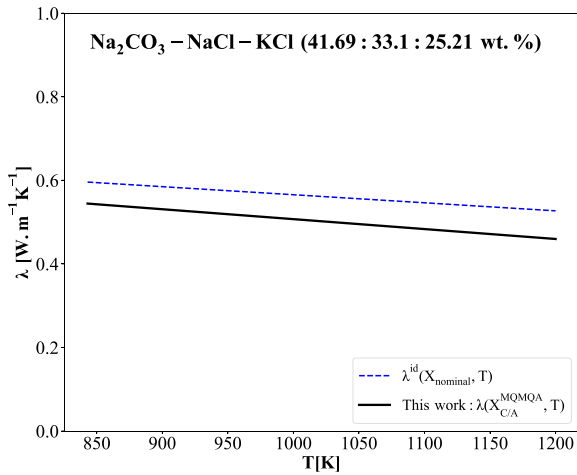


Fig. 9. Predicted thermal conductivity values for reciprocal Na_2CO_3 - NaCl - KCl (41.69:33.1:25.21 wt% or 0.303:0.436:0.261 in mole fraction) molten mixture as a function of temperature for the designed composition compared to the ideal mixing rule estimations.

have influenced these outcomes, as a similar issue was observed in the reciprocal mixture of (Li^+ , Na^+ / F^- , Cl^-). These two observations, however, require validation through further investigations with additional reciprocal mixtures.

Table 3 presents a comparison between the ionic fractions of the mixture and the pair fractions calculated using the MQMQA approach at 1300 [K]. Since the ionic fractions are identical to those in **Table 2**, the random mixing fractions remain unchanged and are not repeated here. However, a comparison between the two tables reveals that for the nominal composition of $(\text{LiF})_{0.5} - (\text{NaCl})_{0.5}$, and $(\text{LiF})_{0.5} - (\text{KCl})_{0.5}$, the pair fractions of Li^+ , K^+/F^- , Cl^- is larger than that of Li^+ , Na^+ / F^- , Cl^- , which can be attributed to the greater magnitude of $|\Delta g^{\text{EX}}|$.

c. (Na^+ , K^+) / (F^- , Cl^-) reciprocal mixture

Fig. 4 presents a comparison between the calibrated predictions (red dashed line) and the EMD results, demonstrating good agreement for both reciprocal mixtures, NaF - KCl and KF - NaCl . The black solid line represents the predictions from the present model at 1300 [K]. In the absence of LiF in the solutions, the predicted values are in closer alignment with the EMD data. In the KF - NaCl mixture, the deviation is relatively small, because of the insignificant difference in thermal conductivity between the two pure end-members and in their molar masses. Furthermore, as shown in **Table 4**, the pair fractions in this mixture exhibit less deviation from random mixing compared to the other two reciprocal mixtures, indicating a smaller Gibbs energy of exchange interaction, with $|\Delta g_{\text{NaK/FCl}}^{\text{EX}}| = 22$ [kJ/mol]. Which reveals that the effect of FNN short-range ordering on thermal conductivity is less significant in this melt.

In summary, this current model demonstrates strong predictive capability of thermal conductivity for reciprocal mixtures with high accuracy, in consistency with EMD results. However, for mixtures

containing LiF , the predicted results were somewhat underestimated compared to the EMD results. This understatement may be due to the overestimated value of pure LiF , which is non-polarizable. This may also be attributed to interatomic interactions between different cations and anions, potentially reducing the effects of mass fluctuation. Overall, predictions for the three reciprocal mixtures show less than 20% error compared to EMD simulations. Consequently, this model shows promise for predicting thermal conductivity in other reciprocal molten salt mixtures across temperatures and compositions with a error of less than 20%. In addition, it is also expected to be applicable to polyatomic salt mixtures such as nitrates and carbonates. The additional predicted compositions for these three reciprocal mixtures align with the EMD results, which are provided in **Appendix A**.

6.1.2. Reciprocal salt mixtures in energy applications

Two reciprocal molten salt mixtures relevant to energy applications have been identified in the literature: HITEC salt ($(\text{NaNO}_3)_{0.07} - (\text{NaNO}_2)_{0.53} - (\text{KNO}_3)_{0.40}$ weight fraction, or 0.066:0.616:0.318 in mole fraction) and $(\text{NaCl})_{0.48} - (\text{KCl})_{0.36} - (\text{NaF})_{0.16}$ (mole fraction). In this subsection, we evaluate the predictions of the current model by comparing them to experimental data from both mixtures.

HITEC salt is one of the most interesting heat transfer fluids in heat recovery process since several decades, it was also the HTF in the test concentrating solar power in Themis. Various experimental measurements of thermal conductivity have been performed since half a century. In **Fig. 5**, we can observe that these experimental results showed a non-positive slope with temperature, which were considered as reliable measurements. The HITEC salt mixtures consists of Na^+ , K^+ , NO_3^- , and NO_2^- , as both the cations and anions are neighboring elements, relatively heavy ions. The mass fluctuation term (Γ) is relatively small. In the MQMQA approach, the pair fractions are 0.2442 for NaNO_3 , 0.2671 for KNO_3 , 0.3139 for NaNO_2 , and 0.1748 for KNO_2 at 430 [K]. In comparison, the pair fractions in Temkin model are 0.285, 0.226, 0.273, 0.216, respectively. The predictions of the current model are represented by the black solid line, compared to the solution based on the ideal mixing rule. As shown in the figure, the predictions of the current model are consistent with the ideal mixing rule. It is worth noting that the model demonstrates better accuracy, showing excellent agreement with the experimental results reported by Odawara et al. [55], Omotani et al. [57], and Le Brun et al. [59]. This is to be understood within the challenging context of experimentally determining thermal conductivity at high temperatures, where even recommended datasets can show deviations of up to 31% for the HITEC salt between investigators for the HITEC salt. Even more so, if the measurements were conducted under ambient conditions, NaNO_2 is unstable in the presence of air (O_2) at high temperatures, leading to the formation of NaNO_3 instead of maintaining the initial weight fractions, which will could further distort the result.

The ternary NaCl - KCl - NaF eutectic salt mixtures was proposed by Wang et al. [89] for the design of a thermo-economical candidate PCMs for next generation CSP plants with supercritical CO_2 Brayton cycle. The thermal diffusivity (α) of this salt mixture was experimentally measured using the laser flash analysis technique. The thermal conductivity was then calculated [89] using the corresponding equation $\lambda = \rho C_p \alpha$.

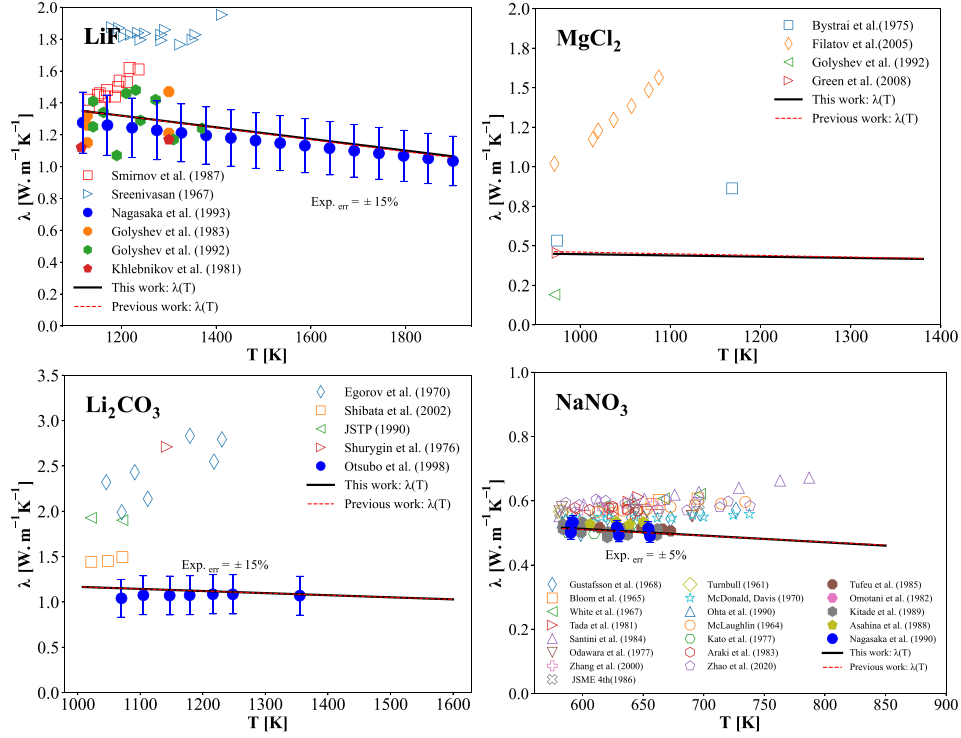


Fig. 10. Predicted thermal conductivity for four pure molten salts of monovalent LiF, divalent MgCl_2 , Li_2CO_3 , and NaNO_3 using the present model, compared to previous work [34], and experimental works reported by Smirnov et al. [12], Sreenivasan [60], Nagasaka et al. [8,42], Golyshev et al. [49,50], Khlebnikove et al. [48], Bystrai et al. [61], Filatov et al. [62], Green et al. [63], Egorov et al. [64], Shibata et al. [65], Shurygin et al. [66], Otsubo et al. [45], Gustafsson et al. [67], Bloom et al. [68], White et al. [69], Tada et al. [47], Santini et al. [70], Odawara et al. [55], Zhang et al. [71], JSME [72], Turnbull [53], McDonald and Davis [73], Ohta et al. [74], McLaughlin [75], Kato et al. [76], Araki et al. [77], Zhao et al. [78], Tufeu et al. [58], Omotani et al. [57], Kitade et al. [38], and Asahina et al. [79].

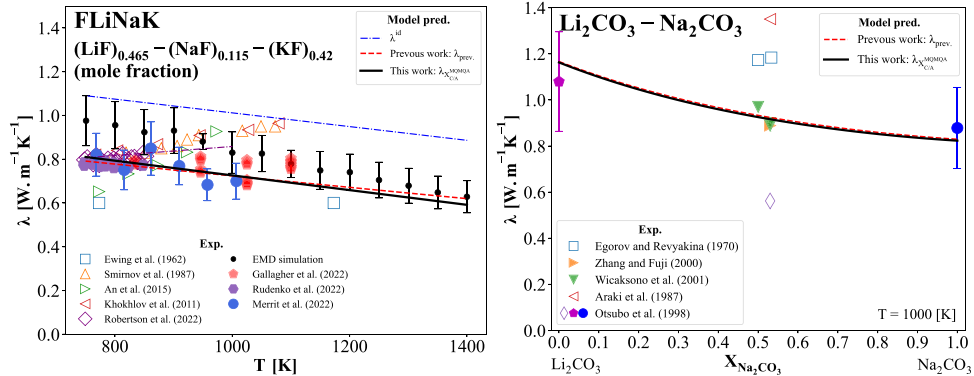


Fig. 11. Predicted thermal conductivity of common-anion molten salt mixtures of FLiNaK as a function of temperature, and Li_2CO_3 - Na_2CO_3 as a function of composition at 1000 [K]. The predictions of the present model (black solid line) are compared with the previous model (red dashed line) [21], and experimental works reported by Ewing et al. [80], Smirnov et al. [12], An et al. [7], Khokhlov et al. [81], Roberston et al. [52], Gallagher et al. [5], Rudenko et al. [82], Merrit et al. [83], Egorov et Revyakina [64], Zhang and Fuji [84], Wicaksono et al. [85], Araki et al. [77], and Otsubo et al. [45]. The datasets for FLiNaK reported by Lane et al. [86] and Janz [87] are not included in the figure.

Table 4

Comparison of different ionic fractions of Na^+ , K^+ / F^- , Cl^- with their corresponding random mixing fractions and pair fractions estimated by the MQMQA approach at 1300 [K].

Cationic and anionic fractions	Fractions	NaF	KF	NaCl	KCl
0.75 Na^+ , 0.25 K^+ /0.75 F^- , 0.25 Cl^-	FNN per MQMQA	0.5819	0.1681	0.1681	0.0819
0.75 Na^+ , 0.25 K^+ /0.25 F^- , 0.75 Cl^-	FNN per MQMQA	0.2010	0.5490	0.0490	0.2010
0.5 Na^+ , 0.5 K^+ /0.5 F^- , 0.5 Cl^-	FNN per MQMQA	0.2759	0.2241	0.2241	0.2759
0.25 Na^+ , 0.75 K^+ /0.75 F^- , 0.25 Cl^-	FNN per MQMQA	0.1995	0.0505	0.5505	0.1995
0.25 Na^+ , 0.75 K^+ /0.25 F^- , 0.75 Cl^-	FNN per MQMQA	0.0770	0.1730	0.1730	0.5770

A comparison between experimental measurements and the current model's predictions is shown in Fig. 6. The experimental data show a pronounced positive temperature dependence, with values near the

melting point approximately 100% higher than our model predictions. These results may be unreliable, as DiGiulio and Teja [9] noted that datasets indicating a positive temperature dependence in thermal

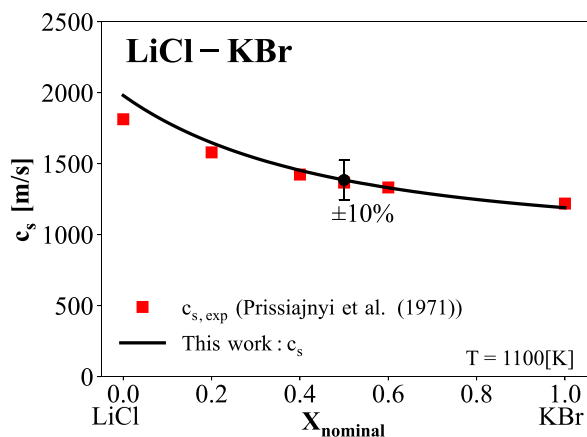


Fig. A.1. Calculated sound velocity from the FTSalt Database of FactSage™ 8.4 for LiCl-KBr as a function of composition at 1100 [K], compared to the experimental data of Prissajnyi et al. [37].

conductivity are potentially inaccurate. For reference, thermal conductivities for the four pure salts from the work of Nagasaka et al. [8,51,90] and the ideal mixing rule solutions are also included, starting from their respective melting temperatures. The experiments by Nagasaka and co-workers are widely regarded as reliable by multiple studies [4, 6,9]. Interestingly, all pure salts exhibit a clear negative temperature dependence, consistent with expected behavior. The pair fractions in the MQMQA approach of each component in this mixture are 0.1185 for NaF, 0.5215 for NaCl, 0.0415 for KF, and 0.3185 for KCl at 1000 [K]. In comparison, the pair fractions estimated by Temkin model are 0.1024, 0.5376, 0.0576, 0.3024, respectively. The predicted results exhibit negative temperature dependence. Furthermore, the values for the mixture lie between those of the pure salts. Based on these findings, we are confident that the current model provides reliable predictions for the ternary mixture $(\text{NaCl})_{0.48}(\text{KCl})_{0.36}(\text{NaF})_{0.16}$ (mole fraction), which are likely more accurate than the experimental results.

6.2. Thermal conductivity predictions for molten salt PCMs

The thermal energy storage system is one of the most critical systems that makes renewable energy plants such as PV, wind, and CSP that provide stable and dispatchable power generation. Nowadays, it has become popular also integrating into conventional power plants to improve the thermal cycle efficiency. Molten salt thermal energy storage systems using PCMs feature a high energy density at high temperatures. However, thermal conductivity, as the key parameter that determines the charging/discharging performance, their knowledge is still very limited. Opolo et al. [91] and Lin et al. [92] reviewed the different molten salts that serve as latent heat thermal energy storage medium. Unfortunately, some of thermal conductivity values is not available, particularly for the reciprocal molten salt mixtures, such as the thermal conductivity values of the eutectic compositions of LiNO_3 -NaCl, LiNO_3 -KCl, and Na_2CO_3 -NaCl-KCl, are unavailable either experimentally or as estimates. Here, we would like to employ the current model to predict the liquid salt as temperature and composition dependence.

In the reciprocal mixture of LiNO_3 -NaCl, the solution products are LiCl, LiNO_3 , NaCl, NaNO_3 (other products such as NaNO_2 , NaClO_4 , LiNO_2 , and LiClO_4 are listed in the FTSalt Database, but their concentrations appear to be negligible, on the order of 10^{-7} , therefore, they were neglected in the predictions). Fig. 7 presents the predicted values as a function of composition and temperature. The temperature was set to 1100 [K], slightly above the melting point of NaCl. Composition-dependent behavior closely follows the ideal mixing rule, as the molecular weights and thermal conductivities of the four components show

no significant differences. A very slight positive deviation may arise from minor inaccuracies in the input properties. The predicted thermal conductivity of LiNO_3 -NaCl (87:13 wt% or 0.85:0.15 in mole fraction) mixture at 496 [K] is to be approximately $0.599 [\text{W}\cdot\text{m}^{-1}\text{K}^{-1}]$. At this temperature, the FNN pair fractions in the MQMQA model are 0.1072 for LiCl, 0.7429 for LiNO_3 , 0.0427 for NaCl, and 0.1072 for NaNO_3 .

Fig. 8 illustrates a similar reciprocal salt mixture, LiNO_3 -KCl, showing the predicted values as a function of composition and temperature. The predicted values align closely with the behavior described by the ideal mixing rule, because of the close values of the molecular weights and thermal conductivities. These outcomes further support the statement that molten mixtures of lithium, sodium, and potassium nitrate salts can be estimated with good accuracy using the ideal mixing rule, as reported by DiGuilio and Teja [9]. The thermal conductivity of LiNO_3 -KCl (58.1:41.9 wt% or 0.6:0.4 in mole fraction) is approximately $0.564 [\text{W}\cdot\text{m}^{-1}\text{K}^{-1}]$ at 445 [K]. The FNN pair fractions obtained from the MQMQA model at this temperature are 0.2180, 0.3819, 0.1821, and 0.2180 for LiCl, LiNO_3 , KCl, and KNO_3 , respectively.

The last reciprocal mixture examined consists of ternary mixtures of Na_2CO_3 -NaCl-KCl with a composition of 41.69:33.1:25.21 wt% or 0.303:0.436:0.261 in mole fraction. In the MQMQA model, the FNN pair fractions at 845 [K] are 0.4070 for NaCl, 0.3036 for Na_2CO_3 , 0.2093 for KCl, and 0.0802 for K_2CO_3 . The thermal conductivity values are approximately 10% lower than those predicted by the ideal mixing rule, as shown in Fig. 9, which primarily results from the significant mass and thermal conductivity difference between carbonate salt and chloride salt, as well as the FNN pair fractions. The thermal conductivity at 845 [K] is estimated to be approximately $0.544 [\text{W}\cdot\text{m}^{-1}\text{K}^{-1}]$. The predictions of the current model could be assumed comparable to reliable experimental measurements. Further experimental work is recommended to support our predictions.

7. Comparisons of predictions from the present model and previous model

In our previous models [21,34] for estimating thermal conductivity, parameters such as thermal expansivity, bulk modulus, Grüneisen parameter, sound velocity, etc were evaluated at the melting point rather than at the actual molten salt temperature. In this work, we consider the actual temperature and estimate these parameters by incorporating additional models. Which not only simplifies the application but also leads to a more accurate estimation of thermal conductivity.

To further emphasize the predictive capability and accuracy of the current model, we will compare the predicted thermal conductivity of randomly selected pure molten salts and common-anion molten salt mixtures with the values obtained from previous models [21,34]. Fig. 10 compares the thermal conductivity predictions from the current model (black solid line) with those from the previous model for pure molten salts (red dashed line). The comparison is made for four pure unary salts: monovalent LiF, divalent MgCl_2 , and lithium carbonate, and sodium nitrate. The analysis of the experimental datasets is not repeated here, please refer to the previous work [34]. These four subfigures demonstrate that the predicted accuracy is consistent with the previous model. However, the predictive capability of the current model is enhanced, as it does not require the melting temperature, unlike the previous model. This feature is particularly advantageous for molten salt mixtures, as their liquidus temperature is typically lower than the melting temperature of pure salts.

The predicted thermal conductivity from the current model (black solid line) is shown in Fig. 11 for two commonly studied common-anion molten salt mixtures: Li_2CO_3 - Na_2CO_3 (composition dependent) and FLiNaK (temperature dependent). The predictions are compared with those obtained from the previous model for common-anion molten salt mixtures (red dashed line) [21]. Both mixtures show results that closely align with previous work. However, the FLiNaK mixture exhibits a slight deviation at high temperatures (above 1200 [K]), which may be

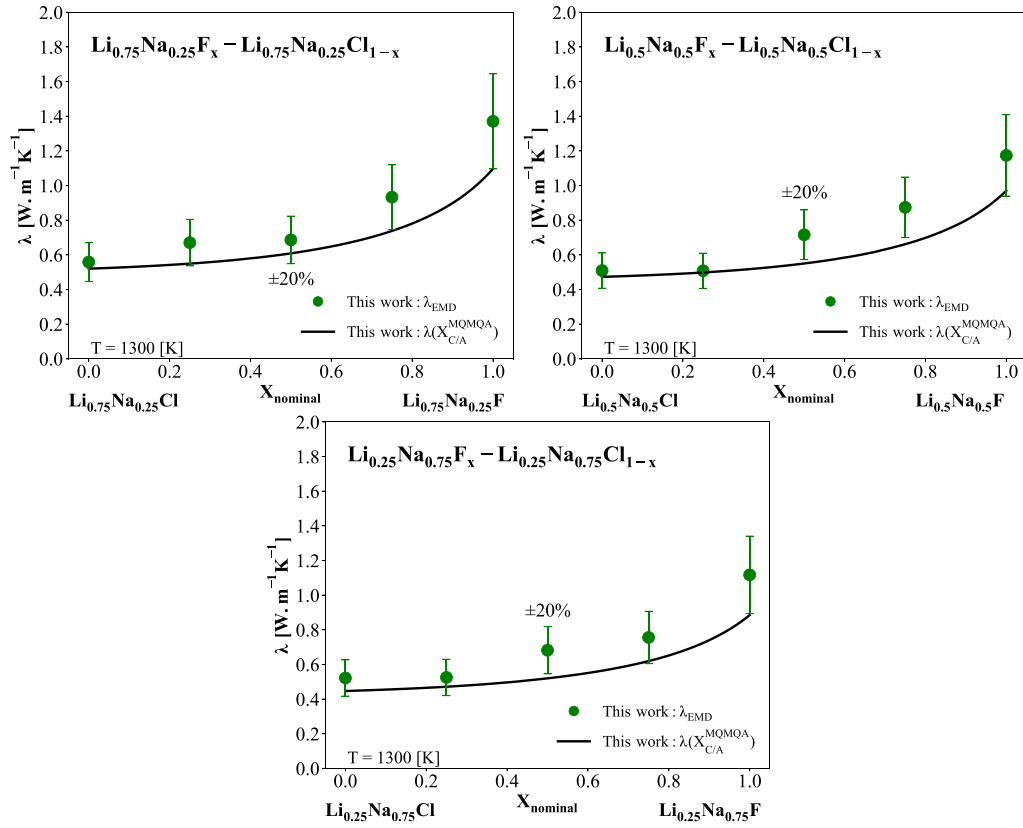


Fig. A.2. Predicted thermal conductivity values of reciprocal Li^+ , Na^+ / F^- , Cl^- molten mixture in comparison to EMD results by this work at 1300 [K].

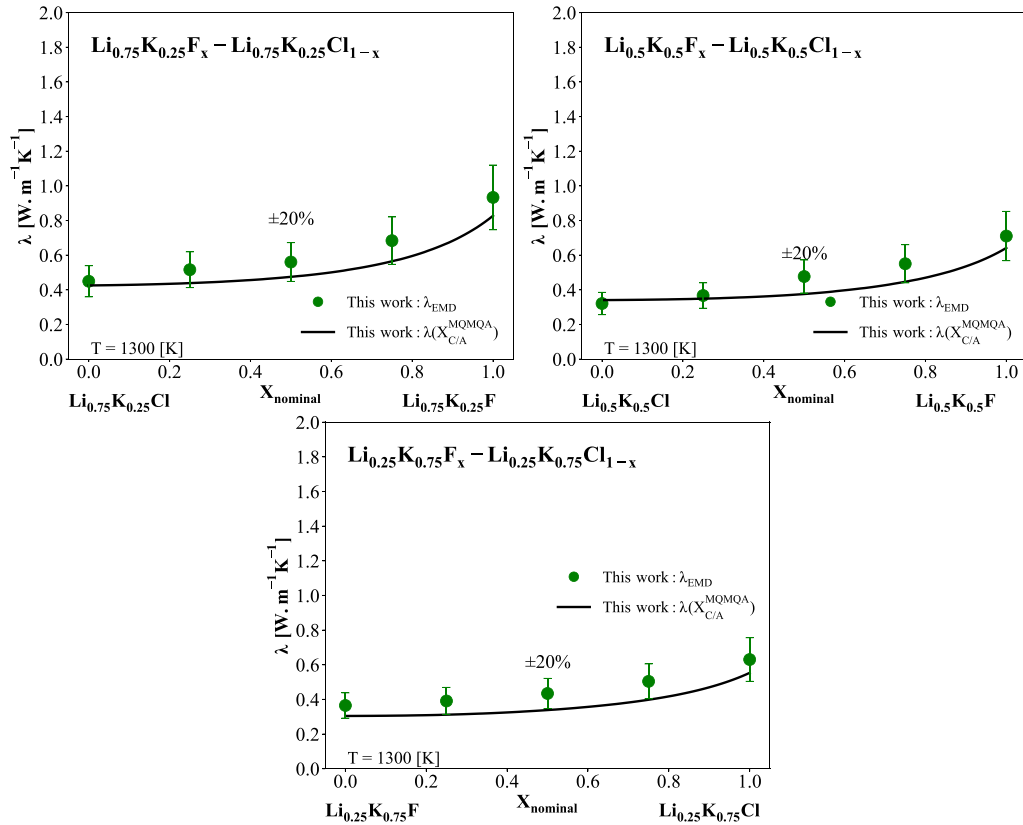


Fig. A.3. Predicted thermal conductivity values of reciprocal Li^+ , K^+ / F^- , Cl^- molten mixture in comparison to EMD results by this work at 1300 [K].

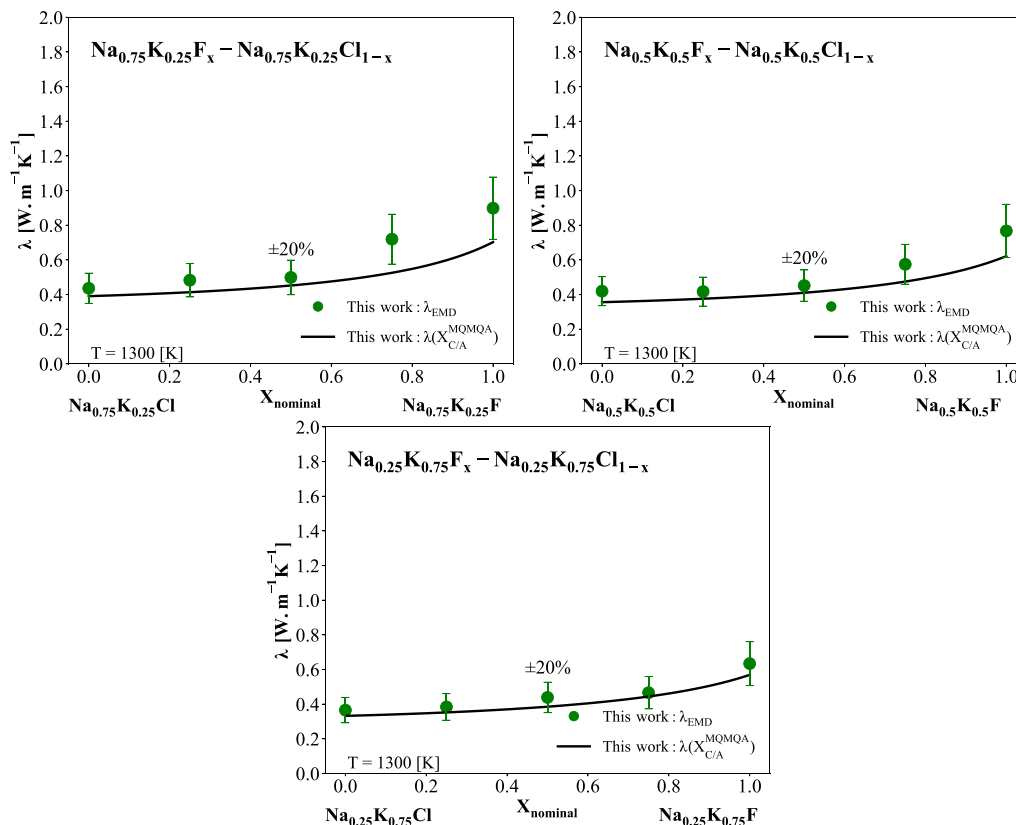


Fig. A.4. Predicted thermal conductivity values of reciprocal Na^+ , K^+ / F^- , Cl^- molten mixture in comparison to EMD results by this work at 1300 [K].

attributed to the assumption of ideal linear variation in the composition of thermal expansion and isothermal compressibility in the previous model. Indeed, the current model appears to be more consistent with the recommended experimental data for FLiNaK. In the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ mixture, it can be observed that the deviations are identical to the results obtained from the previous model. This, in turn, explains that the pair fractions in the MQMQA approach used in the current model are equal to the nominal fractions for common-ion molten salt mixtures. In other words, the current model is identical to the previous model for common-ion molten salt mixtures. Overall, the present model has shown enhanced predictive capability and improved accuracy.

8. Conclusion

In this study, we extended our previously developed kinetic-based thermal conductivity model, initially developed for common-anion mixtures, to include reciprocal molten salt mixtures. This extension incorporates the effects of FNN short-range ordering interactions between cation–anion pairs, using the MQMQA approach. This adaptation is crucial because directly applying nominal mole fractions to reciprocal salt mixtures poses a fundamental challenge: a specific (equivalent) ionic fraction can correspond to an infinite number of possible nominal mole fractions in reciprocal salt solutions.

Thermal conductivity is one of the most difficult parameters to determine, both experimentally and through EMD simulations. Only two experimental studies on reciprocal mixtures were found in the literature, and there is currently no model available that describes the thermal conductivity of reciprocal molten salt mixtures. Numerous EMD simulations of Li^+ , Na^+ , K^+ / F^- , Cl^- mixtures were conducted to validate the present model. The predicted results showed good agreement with EMD results, with a predictive error of up to 20%. The

predictions for HITEC salt align well with reliable experimental measurements, confirming the model's suitability for polyatomic reciprocal salt mixtures.

The model requires only a few thermophysical parameters, such as heat capacity, density, and sound velocity, and exhibits strong predictive capabilities for reciprocal salt mixtures, also including both common-anion and common-cation mixtures. This was demonstrated through its predictions of thermal conductivities for reciprocal molten salt PCMs suggested in the literature as a function of composition and temperature. We expect that the current model will also be able to predict thermal conductivity in other heavy-ion and complex anionic reciprocal salt mixtures. We believe that this work will make a significant contribution to the assessment of thermal conductivity in molten salt mixtures for engineering applications, providing valuable reference data for molten salt databases. Future work will focus on extending the model to molten salt solid solutions.

CRediT authorship contribution statement

Huiqiang Yang: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Anh-Thu Phan:** Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Aïmen E. Gheribi:** Resources, Investigation, Funding acquisition, Data curation. **Patrice Chartrand:** Writing – review & editing, Project administration, Methodology, Funding acquisition, Formal analysis.

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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Appendix A

Using Eq. (12), the sound velocity values for the reciprocal molten salt mixture LiCl–KBr were calculated based on the FTSalt Database of FactSage™ 8.4, and compared with the experimental data reported by Prissiajnyi et al. [37] at 1100 [K]. The predictions closely follow the trend of composition variation observed in the experimental work. In particular, at $X_{\text{nominal}} = 0.5$, our prediction is nearly identical to the experimental results. However, there is a slight deviation for pure molten LiCl. Additionally, sound velocity calculations for various pure molten salts and mixtures have been compared with available experimental datasets, which are provided in Supplementary Materials.

The following figures (Figs. A.2, A.3, A.4) offer additional comparisons between EMD results and the predictions of the present model, further demonstrating its predictive capability. In each figure, the end members correspond to common-anion mixtures. Notably, these figures do not include calibration of thermal conductivity values for the end members (previously indicated by red dashed lines). Instead, only the predictions from the current model (black solid line) are directly compared with the EMD results, demonstrating a strong agreement in trends between the two datasets. This further reinforces the accuracy and reliability of the present model.

Appendix B. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.solmat.2025.113724>.

Data availability

Data will be made available on request.

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