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Recommended values for the thermal conductivity of molten salts between the melting and boiling points

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ABSTRACT

A model for the prediction of the thermal conductivity of molten alkali and alkaline earth salts is proposed. The model is a function of simple thermophysical properties of salts. The parameters required in the calculations are density, heat capacity, velocity of sound and melting temperature. Predictions are in good agreement with reliable experimental and molecular dynamics simulation data. The model displays the correct dependence of the thermal conductivity on temperature, and this is a useful method for a first evaluation of future experimental data.

1. Introduction

The thermal conductivity of molten materials is a critical property for the efficient design of chemical process and equipment. This is particularly true in sectors such as metallurgy, high temperature batteries, waste treatment, heat exchange and solar power technology. For example, the development of technologies for storage of thermal and solar energy over a wide temperature range has become a very topical issue for energy-saving in many industrial sectors [1]. Thus, the accurate knowledge of thermal conductivity of potential heat storage salts such as halides, hydroxides, nitrates, carbonates and others is of first importance to optimize equipment design.

However, thermal conductivity (indicated by λ in this work) of high temperature melts is a very difficult property to measure. Additionally, experimental data for molten salts are very scattered and the number of reliable data sets is very limited. Some indicate positive temperature dependence on thermal conductivity, whereas others show the opposite. Fig. 1 illustrates this situation for the case of molten potassium chloride. This example includes both experimental and estimated data.

Common error sources are temperature variation, convection (inside the fluid and losses by convection) and losses by radiation (thermal radiation). Convection and radiation reduces the energy transferred by conduction given that part of the energy is transferred into the fluid and its surroundings [15–17]. These difficulties have prompted the development of different classes of models [18]. Since 1980s, new measurement techniques have been developed to produce more reliable data sets. These techniques include the Forced Rayleigh Scattering Method and the Transient Hot-Wire technique with ceramic coated probes [15,19]. However, it has been suggested that no single method provides experimental uncertainty less than 5% [20].

Earlier data sets show much scatter with $d\lambda/dT > 0$. More recent data sets show $d\lambda/dT < 0$, which is normal for simple liquids. Thus, temperature dependence becomes a simple way to evaluate the reliability of data [18]. As discussed by DiGuilio and Teja [18], molten salts have very simple structures. Thus, it would be expected that $d\lambda/dT$ would be negative along the saturation curve, in common with other simple liquids. This assumption has been supported by results obtained from more recent techniques such as the Forced Rayleigh Scattering Method and the Transient Hot-Wire technique with ceramic coated probes which show the correct negative temperature dependence [15,21,19]. These techniques have been developed to minimize error sources such as convection, temperature variation and losses by radiation [16,17]. Results from Molecular Dynamics Simulation also support the behavior $d\lambda/dT < 0$ [11,14,22,23].

Several kinds of models have been proposed to estimate the thermal conductivity of melts. Some are empirical models which have limited application for prediction [24–26]. The principle of corresponding states has also been used to estimate the thermal

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Nomenclature

λ	thermal conductivity (W/m/K)
T	temperature (K)
ρ	density (Kg/m^3)
P	pressure (Pa)
α	Thermal expansivity (K^{-1})
ν	average lattice vibrational frequency (s^{-1})
γ	Gruneisen parameter (Dimensionless)
T_{fus}	melting temperature (K)
λ_{fus}	thermal conductivity at T_{fus} (W m/K)
α_{fus}	thermal expansivity at T_{fus} (K^{-1})
γ_{fus}	Gruneisen parameter at T_{fus} (Dimensionless)
ρ_{fus}	density at T_{fus} (Kg/m^3)
U_{fus}	velocity of sound at T_{fus} (m/s)
V_{fus}	molar volume at T_{fus} (m^3/mol)
M_w	molecular weight (Kg/mol)
C_p	molar constant pressure heat capacity (J/mol/K)
$C_{p,fus}$	molar constant pressure heat capacity at T_{fus} (J/mol/K)
$\overline{C_V}$	volumetric constant volume heat capacity (J/m^3/K)
C_V	molar constant volume heat capacity (J/mol/K)
$C_{V,fus}$	molar constant volume heat capacity at T_{fus} (J/mol K)
$\langle l \rangle$	phonon mean free path (m)
r_a	anionic radius (m)
r_c	cationic radius (m)
n	number of atoms per molecule
K	constant (Dimensionless)

conductivity of molten salts with relatively good results [27–30]. However, this requires knowledge of specific parameters for each compound which are not always available. DiGuilio and Teja [18] proposed a model based on the hard-sphere theory. This model was tested in the prediction of thermal conductivity of molten chlorides and nitrates with good results. However, the behavior of one single member of each common anion family must be known in order to obtain estimations for the other members. As mentioned, reliable data sets are not readily available for each family of molten salts; this imposes some limitations in the use of this model. The last kind of model is a group of the predictive and semi-empirical models [18,31,32]. These models are based on physical theories and involve a variety of physical properties such as molar volume, heat capacity, velocity of sound and melting temperature. They usually include a fitting parameter which is particular to the substance of interest. More recently, molecular dynamics (MD) has also been used to predict thermal conductivity of molten salts with relatively good success [11,14,22,23]. However, calculations are time-consuming and quite complicated.

In this work, we present a new and simple predictive model to estimate the thermal conductivity of molten salts based on simple physical properties. Only the density, velocity of sound, heat capacity and the melting temperature of the molten salt are required to estimate the temperatures dependence of the thermal conductivity. The model is based on the assumption that thermal conductivity of melts depends strongly on density but weakly on temperature. This assumption is supported by conclusions from molecular dynamics calculations performed for molten alkali halides [11]. Results are compared with the most reliable experimental data sets available in the literature (obtained from most recent optical and transient techniques and showing the correct negative temperature dependence).

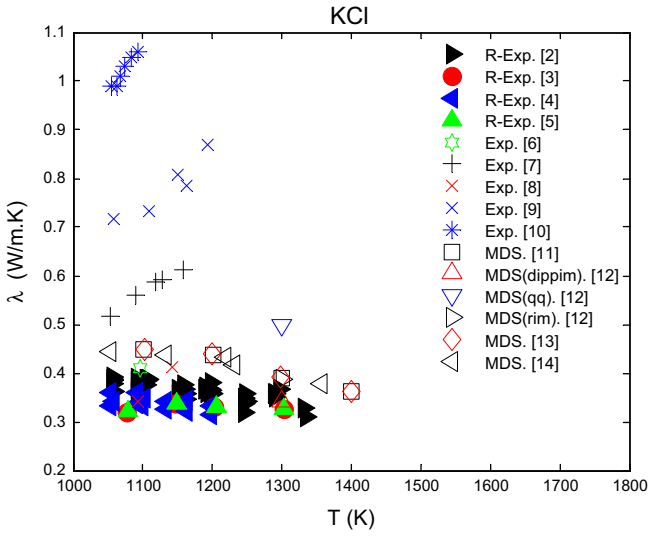

Fig. 1. Available experimental and molecular dynamics simulation (MDS) data for thermal conductivity of molten KCl [2–14]. Most reliable experimental data are identified by 'R' and filled markers. Molecular dynamics results are identified by MDS. Other experimental data are considered not reliable.

2. Proposed model for prediction of the thermal conductivity

2.1. Temperature dependence

Ohtori et al. [11] suggested that $d\lambda/dT$ behavior of molten salts at constant pressure is determined mainly by the temperature dependence of the density. Thus, the thermal conductivity of molten salts does not depend significantly on temperature but on the coefficient of thermal expansivity. This assumption can be represented by:

$$\left(\frac{\partial \ln\lambda}{\partial T}\right)_{\rho} = 0 \tag{1}$$

Based on this assumption, we propose a new model to predict the temperature dependence of thermal conductivity of molten salts. The model is derived as follow:

Using thermodynamics and after Legendre Transformation, it is possible to show that [33]

$$\left(\frac{\partial \ln\lambda}{\partial T}\right)_{P} = \left(\frac{\partial \ln\lambda}{\partial T}\right)_{\rho} + \left(\frac{\partial \ln\rho}{\partial T}\right)_{P}\left(\frac{\partial \ln\lambda}{\partial \ln\rho}\right)_{T} \tag{2}$$

Table 1
Values of ionic radii suggested to be used in Eq. (18) [37,38].

Cationic radii r (Å)				Anionic radii r (Å)		Effective anionic radii (Å)	
Li^+	0.76	Be^{2+}	0.45	F^-	1.33	CO_3^{2-}	2.65
Na^+	1.02	Mg^{2+}	0.72	Cl^-	1.81	NO_3^-	2.31
K^+	1.38	Ca^{2+}	1.00	Br^-	1.96	NO_2^-	2.50
Rb^+	1.52	Sr^{2+}	1.18	I^-	2.20	SO_4^{2-}	3.18
Cs+	1.67	Ba^{2+}	1.35	–	–	OH^-	1.10