

## **A Rough Hard-Sphere Model for the Thermal Conductivity of Molten Salts**

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A new model based on the rough hard-sphere theory is proposed for the correlation and prediction of the thermal conductivity of molten salts. The model is capable of predicting the thermal conductivity of all the members of a family of molten salts characterized by a common anion if the behavior of any single member of the family of salts is known. Only the molar volumes of the molten salt and the solid salt at the melting temperature are required in the calculations. In addition, the model is easily extended to mixtures with a simple mixing rule.

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**KEY WORDS:** kinetic theory; molten salts; thermal conductivity.

### **1. INTRODUCTION**

Molten salts offer a unique opportunity to evaluate theoretical and semi-theoretical models of thermophysical properties because of the simplicity of their structures. Unfortunately, the difficulty in measuring the properties of molten salts makes it difficult to find reliable data with which to test such models. This is especially true in the case of the thermal conductivity. Recently, Nagasaka and Nagashima [1] evaluated all the available thermal conductivity data for molten  $\text{NaNO}_3$  and  $\text{KNO}_3$  and recommended standard data sets for these two salts. Moreover, we have recently measured standard quality data for the  $\text{NaNO}_3$ - $\text{KNO}_3$  eutectic using a new transient hot-wire method [2]. The availability of critically evaluated standard data provides an opportunity to reexamine the problem of modeling the thermal conductivity of molten salts.

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In this study, the temperature and pressure behavior of molten salts is established and available models for the thermal conductivity are reviewed. Finally, a new model for the thermal conductivity of molten salts based on the rough hard-sphere theory of Li et al. [3] is proposed.

## 2. THE BEHAVIOR OF THE THERMAL CONDUCTIVITY OF MOLTEN SALTS

The thermal conductivity of argon is sketched in Fig. 1 (see Ref. 4 for a more detailed plot) and shows that the thermal conductivity of the liquid along the saturation curve decreases slowly with temperature until the critical region is reached. In the critical region, the thermal conductivity drops rapidly and that of the gas increases rapidly until  $\partial\lambda/\partial T = \infty$  at the critical point. This temperature behavior along the saturation line is typical of many liquid substances, the only known fluids to show exception to this behavior being highly hydrogen-bonded fluids such as water and ethylene glycol. The thermal conductivity of water is sketched in Fig. 2 [5] and shows that the value first increases with temperature and then decreases until the critical point is reached. The most likely explanation of this behavior is that hydrogen bonds cause the formation of a structure which somehow facilitates heat transfer. Above about 408 K, thermal agitation breaks up the structure and the usual behavior for liquids is followed (i.e., liquid thermal conductivity decreases with temperature).

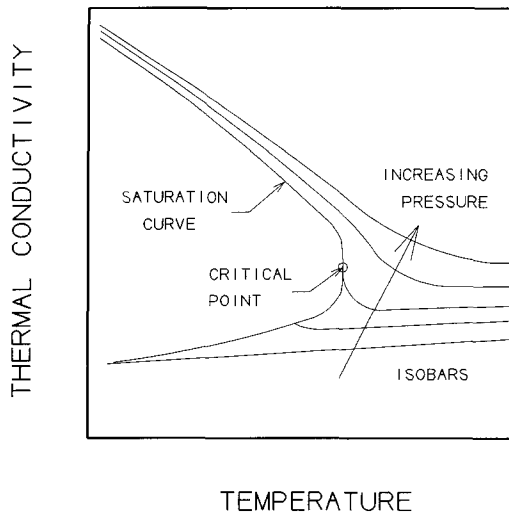


Fig. 1. The thermal conductivity surface of argon.

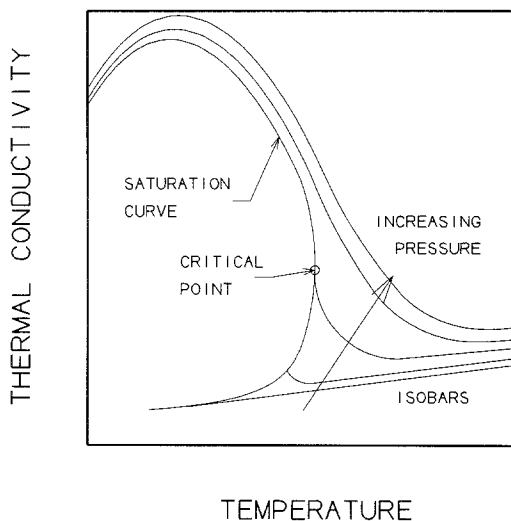


Fig. 2. The thermal conductivity surface of water.

Knowing that examples of both negative and positive temperature dependence exist, we now consider molten salts. Since the structures of molten salts are so simple, we expect the thermal conductivity along the saturation curve to follow the behavior of argon and have a negative dependence on temperature. However, the effect of the electrical charges

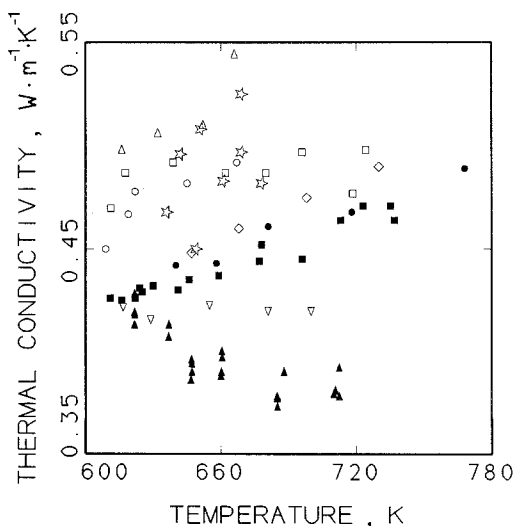


Fig. 3. Thermal conductivity of molten  $KNO_3$ .

complicates this picture. If we consider the experimental data for a molten salt such as  $\text{KNO}_3$ , shown in Fig. 3, we see that investigators do not agree on the temperature dependence. Some results show an increase, whereas other results show a decrease, in the thermal conductivity with increasing temperature. Even for a simple liquid such as toluene, convection and radiation contributions caused early investigators to get erroneously large values for the thermal conductivity [2]. We can speculate the same happening to the early molten salt investigators. Convection is more likely to occur with an increase in temperature because of a decrease in the fluid density. Golyshev et al. [6] showed that the radiation contribution could give rise to an erroneous positive temperature dependence, the slope of which was a function of the emissivity of the walls of the container. This is likely to be true for all the steady-state methods such as concentric cylinders and parallel plates. Thus, if an investigator had problems with convection and radiation, these effects were likely to worsen with temperature and possibly result in a positive temperature coefficient for the thermal conductivity. If we look at Fig. 3 again, but include only the data from 1980 onward as shown in Fig. 4, we see a much different picture. All the data indicate a negative temperature dependence for the thermal conductivity. Thus, apparently, the effect of the electrical charges on the temperature coefficient of the thermal conductivity is negligible. This finding agrees with the statement made by McLaughlin [7] in 1964 on the proper-

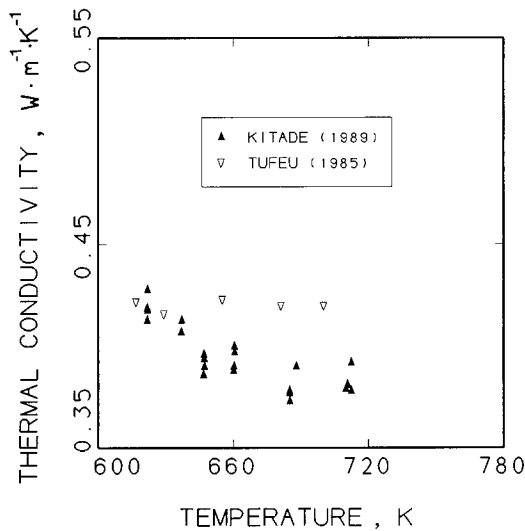


Fig. 4. Thermal conductivity of molten  $\text{KNO}_3$  using post-1980 measurements.

ties of molten salts: "With regard to transport properties there is no evidence that either the viscosities, diffusion coefficients, or thermal conductivities are substantially different from those of ordinary simple liquids." The hypothesis that molten salts should behave like simple liquids is the basis for many models (including the one to be proposed here). Thus, temperature dependence provides an easy check on the reliability of data. If the temperature dependence is positive, and the measurement technique was some kind of steady-state method, then the data are probably wrong. An example is shown in Fig. 5. The data of Smirnov et al. [8], taken in 1987 with a steady-state concentric-cylinder apparatus, show a positive temperature dependence, while those of Nakazawa et al. [9], measured with a forced Rayleigh scattering technique in 1990, show the correct negative temperature dependence.

Figure 5 demonstrates another general trend about the thermal conductivity of molten salts. For a family of salts with a common ion, the thermal conductivity of the melt decreases with increasing size of the other ion. The data of Smirnov et al. [8] for all the alkali halides show this trend very well.

The effect of increased pressure (or density) on the thermal conductivity of a liquid is clear and is illustrated in Figs. 1 and 2. Increasing the pressure increases the thermal conductivity only slightly. Although the pressure effect has never been studied in molten salts, it is safe to assume

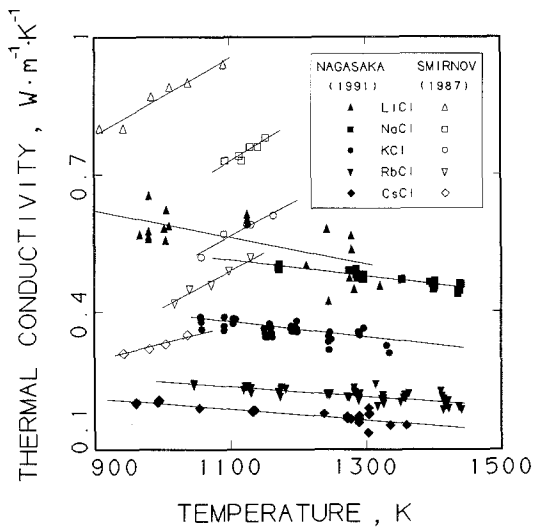


Fig. 5. Thermal conductivity of molten alkali chlorides.

that molten salts behave like all other liquids and that their thermal conductivity increases only slightly with pressure.

Any model developed should include the pressure, temperature, and other effects discussed above.

### 3. REVIEW OF MODELS

The difficulties associated with the measurement of the thermal conductivity of molten salts has prompted the development of many models. The vast majority of models fall into one of three classes. The first class consists of models of the Bridgeman [10] type. The liquid is modeled as a quasi-crystalline substance in which heat travels at the speed of sound. The second class of models also assumes a lattice structure but adopts a more mechanistic approach to the representation of the heat transfer. This class of models is characterized by the splitting of the conduction of heat into vibrational and diffusive contributions. The vibrational component results from higher-energy molecules bumping into lower-energy neighbors. The diffusive component results from high-energy molecules physically moving down the gradient into an area of lower-energy molecules. In a solid, transfer of heat is effected exclusively by the vibrational mechanism. In a gas, transfer of heat is accomplished exclusively by the diffusive mechanism. The third class of models is based on the corresponding-states principle.

The Bridgeman [10]-type equations result from the analysis of the liquid as a lattice. The energy differences between adjacent layers of molecules is transmitted through the lattice in the direction of the gradient at the speed of sound. The expression for the thermal conductivity derived by Bridgeman is given by

$$\lambda = \frac{3kU}{l^2} \quad (1)$$

where  $U$  is the speed of sound,  $k$  is Boltzmann's constant, and  $l$  is the interparticle distance. The interparticle distance  $l$  can be estimated from

$$l = \left( \frac{V}{nN_A} \right)^{1/3} \quad (2)$$

where  $V$  is the molar volume,  $N_A$  is Avogadro's number, and  $n$  is the number of ions per salt molecule. A slight modification of this equation is due to Kincaid and Eyring [11], who included Eucken's correction factor to account for the internal degrees of freedom of polyatomic molecules as follows:

$$\lambda = \left( \frac{0.931}{\gamma^{1/2}} \right) 3k \left( \frac{nN_A}{V} \right)^{2/3} U \quad (3)$$

where  $\gamma = C_p/C_v$ , the ratio of the heat capacity at constant pressure to that at constant volume. Turnbull [12] and Gustafsson et al. [13] found the Bridgeman equation to give values that are too high by about 25% when used for alkali nitrates. Turnbull [12] also found that the Kincaid and Eyring expression works very well for the alkali nitrates (within about 0.5%), while Gustafsson et al. found that it predicts the thermal conductivity of alkali nitrates to within about 7%. The difference is due mostly to the difference in the experimental data with which the models were compared. Recently Nagasaka and Nagashima [1] evaluated the thermal conductivity data available for  $\text{NaNO}_3$  and  $\text{KNO}_3$  and found that the data used by Turnbull and Gustafsson et al. in their comparisons were too high by 10–15%, so the actual accuracy of these models is of the order of 20–40%. Aside from limited accuracy, the most serious problem with the use of these models is the limited availability of speed-of-sound and heat capacity data.

The second class of models considers contributions to thermal conductivity from two sources: (i) a vibrational contribution from heat transfer via colliding molecules and (ii) a diffusive contribution from heat transfer which occurs when high-energy molecules move physically into holes located in regions of fluid with a lower temperature. The thermal conductivity is given as

$$\lambda = \lambda_{\text{vib}} + \lambda_{\text{diff}} = \frac{avC_v}{l} + \frac{2DC_v}{l^2} \quad (4)$$

where  $C_v$  is the specific heat at constant volume,  $\nu$  is the mean vibrational frequency,  $D$  is the diffusion coefficient,  $l$  is the average interparticle distance, and  $a$  is a constant depending on the particular derivation of the vibrational component and is usually taken as 2. The use of Eq. (4) is generally limited to temperatures near the melting point so that the liquid can be considered to have a quasi-crystalline structure. There are two implications of this assumption. The first is that the diffusive contribution to the thermal conductivity should be very small. It was argued by Turnbull [12] that the high ratio of the thermal-to-mass diffusivity (about 70 to 100) is an indication that the diffusive contribution is small. A second point in Turnbull's argument was that the Lorenz ratio, which relates thermal and electrical conductivities, is constant for both solid and liquid metals because electron mobility is responsible for both phenomena. In molten salts, the Lorenz ratio is not constant and is several hundred times the value for metals. Thus, since ionic mobility is the carrier for electrical conduction, it must be unimportant for thermal conduction. According to Turnbull's [12] calculations, the diffusive component contributes less than

4% to the total thermal conductivity. Gustafsson et al. [13] found the diffusive component to be less than 1% of the total. The second implication of the assumed quasi-crystalline structure is that the vibrational frequency,  $\nu$ , can be calculated from simple models such as the harmonic oscillator and the rectangular cell potential model.

The above approach was adopted by Rao [14, 15] in his model. The diffusive component was ignored, the vibrational frequency was taken to be that given by the harmonic oscillator model of Lindemann [16], and the result was

$$\lambda = 6.657 \times 10^{-6} \left( \frac{T_m}{M_w V^{4/3}} \right)^{1/2} \quad (5)$$

where  $\lambda$  is in  $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ,  $T_m$  is the melting temperature in K,  $V$  is the molar volume in  $\text{m}^3 \cdot \text{mol}^{-1}$ , and  $M_w$  is the molecular weight in  $\text{kg} \cdot \text{mol}^{-1}$ . Rao's model is limited to the melting point.

Gustafsson et al. [13] derived a similar model using the rectangular cell potential model of Horrocks and McLaughlin [17] to calculate the vibrational frequency. The result was

$$\lambda = \frac{6k}{2sl} \left( \frac{nN_A}{V} \right)^{1/3} \left( \frac{2kT}{\pi m} \right)^{1/2} \quad (6)$$

where  $V$  is the molar volume in  $\text{m}^3 \cdot \text{mol}^{-1}$ ,  $T$  is in K,  $n$  is the number of ions per molecule,  $sl$  is the interionic distance minus the sum of the radii of the cation and anion in meters, and  $m$  is the molecular mass in kg. For a salt with a single anion and cation,

$$m = (M_a M_c / N_A^2)^{1/2} \quad (7)$$

where  $M_a$  and  $M_c$  are the molecular weights of the anion and cation, respectively. In order to use this model, a choice must be made for the ionic radii. Gustafsson et al. [13] presented a comparison of this model with data for the alkali nitrates using different sources for the ionic radii. Considering that the data with which the model was compared were in error by about 10–15%, the predictions of the thermal conductivity of the nitrates were 10–40% high, depending on the source of the molecular diameter. When the molecular radii of the anions were adjusted to fit the data, the thermal conductivity could be correlated with an average absolute deviation of about 3%. Thus the model does have some correlative ability but little predictive capability.

The third class of models for the thermal conductivity of molten salts is based on corresponding states. White and Davis [18] plotted  $\lambda/\lambda_m$  vs



$\rho/\rho_m$  (where  $\rho$  is the density and the subscript m refers to the liquid at the melting point) for their alkali nitrate data and found all the points to lie on a single line. They also plotted  $\lambda/\lambda_m$  vs  $T/T_m$  and found that each nitrate gave a separate curve. The conclusion was that density was a better reducing parameter in corresponding-states treatments of the thermal conductivity. The White and Davis model had no predictive capability, however. Young and O'Connell [19] chose an arbitrary point along the liquid saturation curve as the reference point and plotted  $\lambda/\lambda^*$  vs  $T/T^*$ , where  $\lambda^*$  is an empirical parameter unique to each salt determined by fitting experimental thermal conductivity data.  $T^*$  was determined for each salt by fitting experimental isobaric-compressibility data at the reference point on the saturation curve. The plot of  $\lambda/\lambda^*$  vs  $T/T^*$  was found to be linear for molten salts that included some alkali halides and the alkali nitrates. The disadvantage is the necessity of having some experimental thermal conductivity data in order to calculate  $\lambda^*$ . Tada et al. [20] used the correlation function expressions for the transport coefficients to derive expressions for the reduced transport coefficient of 1:1 molten salts. However, they cited a lack of reliable data for preventing the application of their results to thermal conductivity. After making new measurements on the thermal diffusivity of the alkali halides, Nagasaka and Nagashima [21] used the formalism of Tada et al. to correlate their data. The plot of reduced thermal conductivity vs reduced temperature was fit with a line which represented the data with a standard deviation of 14% and a maximum deviation of about 30%. One advantage of the correlation was that the four potential parameters required for each salt could be used to correlate transport and equilibrium properties of the salt. These parameters were determined previously for all the alkali halides by Harada et al. [22] with equilibrium data. As a result, Nagasaka and Nagashima were able to make predictions for the thermal conductivity of those molten salts not yet measured. The thermal conductivity of the molten alkali fluorides were estimated with an accuracy of 15 to 20% using this approach.

#### 4. PROPOSED MODEL

It was mentioned earlier that the effect of the charges on the transport properties of molten salts is not large and so it could be expected that molten salts would behave like simple molecules. Because of this premise, the theory of hard spheres was investigated for its applicability to molten salts. The particular model chosen is based on the van der Waals model of a dense fluid. Basically, this model assumes that at sufficiently high densities and temperatures, the actual intermolecular potential can be approximated by a rigid core surrounded by a constant attractive potential.

As pointed out by Li et al. [23], when the van der Waals model is used with the Enskog theory and the results of computer simulation, an explicit prediction of the density dependence of all the transport properties results. However, Li et al. also pointed out that real molecules are not hard spheres and therefore derived an expression for the reduced thermal conductivity of a system of hard spheres as follows:

$$\lambda^* = \frac{64}{75} \left( \frac{m\pi}{k^3 T} \right)^{1/2} \frac{2^{1/3}}{N_A^{2/3}} \lambda V^{2/3} \quad (8)$$

$$= 1.936 \times 10^7 \left( \frac{M_w}{RT} \right)^{1/2} \lambda V^{2/3} \quad (9)$$

where  $m$  is the molecular mass,  $k$  is Boltzmann's constant,  $R$  is the gas constant in  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ,  $T$  is the temperature in K,  $M_w$  is the molecular weight of the undissociated salt in  $\text{kg} \cdot \text{mol}^{-1}$ ,  $\lambda$  is the thermal conductivity in  $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ , and  $V$  is the molar volume in  $\text{m}^3 \cdot \text{mol}^{-1}$ . The interesting characteristic of  $\lambda^*$  is that it is a function of only the molar volume:

$$\lambda^* = F(V/V_0) \quad (10)$$

where  $V_0$  is the molar volume at closest packing. For spheres,  $V_0 = N_A \sigma^3 / \sqrt{2}$ , where  $\sigma$  is the molecular diameter.

It was shown by Chandler [24] that the viscosity of rough hard spheres is related to that of smooth hard spheres by

$$\eta_{\text{RHS}} = C_\eta \eta_{\text{SHS}} \quad (11)$$

where  $C_\eta$ , the translational-rotation coupling constant, is independent of temperature and density. This result suggests that, by analogy, the thermal conductivity of a molten salt is related to that of a smooth monatomic reference liquid such as argon as follows:

$$\lambda_{\text{MS}}^* = C_\lambda \lambda_{\text{Ar}}^* \quad (12)$$

where  $C_\lambda$  is again independent of temperature and density. It is to be expected that  $C_\lambda$  will be a function of each salt. That is, the translation-rotation coupling constant is not expected to have the same value for potassium nitrate as it does for potassium chloride.

In order to test the model, the available data were reviewed and the most reliable data were selected. Unfortunately, this left very few data with which to work. Included were the sodium and potassium nitrate measurements made since 1980 by Kitade et al. [25], Omotani et al. [26, 27], and Tufeu et al. [28]. The selection of these data is in agreement

with the recent recommendations of Nagasaka and Nagashima [1]. Also included were the 1990 measurements of the alkali chlorides by Nakazawa et al. [9] since these were the only data for these compounds that had the correct temperature dependence.

The model was applied in the following way. The quantity  $\lambda^*$  was calculated for each of the experimental points and plotted against the quantity  $(V - V_m)/V_s$ , where  $V_m$  and  $V_s$  are the molar volumes of the liquid and solid, respectively, at the melting point. The molar volume of the solid at the melting point was substituted for the closest packed volume  $V_0$ . The advantage of using  $(V - V_m)$  instead of just  $V$  is that all curves start at the same place, the  $\lambda^*$  axis. Also plotted was the quantity  $\lambda^*$  for argon, xenon, and krypton. The necessary data to calculate these quantities and their sources were as follows. Molar volumes for the molten salts were taken from the compilation of Janz [29]. Solid molar volumes were calculated from the liquid volumes and volume change on fusion data given by Janz. The thermal conductivity of argon, xenon, and krypton were taken from the paper by Roder et al. [30] and the compilation of Touloukian et al. [31]. Molar volumes for the inert gases were taken from Rabinovich et al. [32]. The resulting curves are shown in Fig. 6. The curves for  $\lambda^*$  for the alkali chlorides are parallel to those for the inert gas liquids, indicating that these molten salts have the same density dependence as the inert gas liquids. This would probably hold true for all alkali halides. Since the curve for the inert-gas liquids is established all the

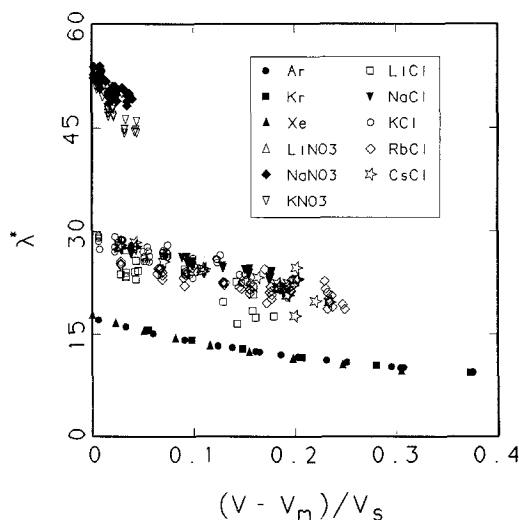


Fig. 6. Plot of  $\lambda^*$  vs  $(V - V_m)/V_s$ .

way up to the critical point, the thermal conductivity of these molten salts can be interpolated or extrapolated with the inert liquid curve. The second success of the model is in capturing the effect of the ion weight on the thermal conductivity. The model collapses the thermal conductivity vs temperature curves for a family of compounds having a common ion onto a single curve. This is shown by both the alkali nitrate and the alkali chloride data. In the case of the alkali halides, the constant  $C_\lambda$  not only is independent of temperature and density but also is constant for each family of compounds characterized by a common ion. The advantage of this situation is that the thermal conductivity of all the members of a family can be predicted with confidence from a single measurement on a single member of the family and the inert liquid curve. In the case of the nitrates, the simple assumption that the quantity  $\lambda_{MS} = C_\lambda \lambda_{Ar}$  may not hold. Nevertheless, with thermal conductivity vs temperature data on only one member of the family of nitrates, all the other nitrates can be predicted.

At the beginning of this paper, it was emphasized that a good model should incorporate the temperature dependence, the pressure dependence, and the effect of the ion weight on the thermal conductivity. This model has incorporated the temperature and pressure (through the density) effects and the ion weight effects. However, there are no data on the thermal conductivity of molten salts under pressure, so that the model cannot be tested for pressure effects. Wakeham [33, 3] has shown that a similar rough hard-sphere model represents very well the effect of pressure on the thermal conductivity for hydrocarbon liquids. The rough hard-sphere model on which this model is based has also been used to find expressions for the other transport properties as shown by Li et al. [23]. The same scheme used here for thermal conductivity could also be applied to other transport properties of molten salts.

To facilitate further the use of the model,  $\lambda^*$  vs  $(V - V_m)/V_s$  for the inert gases was fitted to a polynomial of the form

$$\lambda^* = 17.16279 - 35.13805\zeta + 43.75342\zeta^2 - 18.0089\zeta^3 \quad (13)$$

$$\zeta = \frac{V - V_m}{V_s} \quad (14)$$

Three ways of using the model were compared. The first (Method I) was to find the parameter  $C_\lambda$  for the alkali nitrates and alkali chlorides by finding the optimum parameter for shifting the experimental data for sodium nitrate and sodium chloride to the inert curve given above. These two were chosen to represent their families since their thermal conductivities are the most well established. The other salts could then be predicted using the

Table I. Parameters from Fitting of Data

Class of salt	Method I	Method II <sup>a</sup>		Method III <sup>a</sup>	
	$C_\lambda$	$a$	$b$	$a$	$b$
Alkali nitrates	3.0757	52.791	105.04	52.621	147.53
Alkali chlorides	1.8420	28.005	24.835	27.891	33.343

$$^a \lambda^* = a - b\zeta.$$

appropriate  $C_\lambda$  and the inert liquid curve. The second way (Method II) was to fit only the sodium chloride and sodium nitrate data to a line and to predict the other salts from these correlations. The third (Method III) was to fit all the alkali chloride and alkali nitrate data and examine the goodness of fit. From each of these fits, the thermal conductivity calculated from the model was compared with the data. The first two techniques represent true *predictions* for all the molten salts except the sodium salts. The last technique is simply a correlation of the data. The results of the fits are given in Table I. The results of the comparisons with experimental data are given in Table II. Both the model correlations and the predictions are well within experimental error for the chlorides. For the nitrates, the correlation is within experimental error and the predictions just exceed the claimed accuracy of the data for potassium nitrate. However, the two sets of experimental data for potassium nitrate, Tufeu et al. [28] and Kitade et al. [25] do not agree within their claimed accuracy either. Figures 7 and 8 show graphically the results of the predictions resulting from fitting the

Table II. Model Performance

Molten salt	Claimed accuracy of data (%)	AAD % <sup>a</sup>		
		Method I	Method II	Method III
LiNO <sub>3</sub>	±3	1.0	1.0	1.0
NaNO <sub>3</sub>	±3-4	1.5	1.5	3.7
KNO <sub>3</sub>	±3-4	5.4	5.4	2.1
LiCl	±20	19.4	16.4	12.2
NaCl	±8	3.9	1.2	4.9
KCl	±8	5.5	3.2	4.2
RbCl	±15	9.3	10.2	5.3
CsCl	±18	5.2	5.8	4.0

$$^a 100 \times (|\lambda_{\text{calc}} - \lambda_{\text{expt}}|) / \lambda_{\text{expt}}.$$

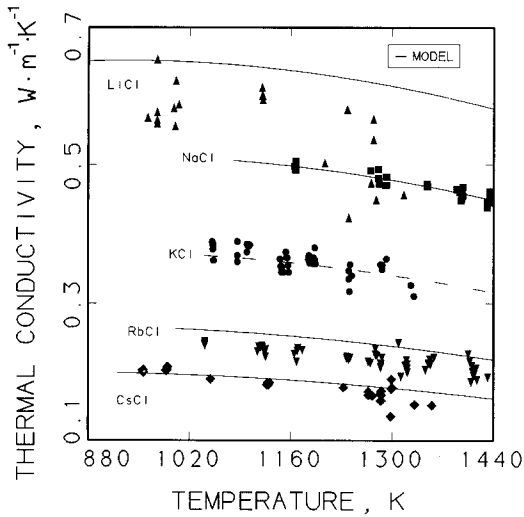


Fig. 7. Prediction of the thermal conductivity of the alkali chlorides from NaCl data.

sodium chloride and nitrate data. Each family of molten salts has been *predicted* with the data from one salt and a model that incorporates both the pressure and the temperature dependence (through their effect on the molar volume) of the thermal conductivity. All predictions appear to be within the estimated accuracy of the experimental results except for LiCl.

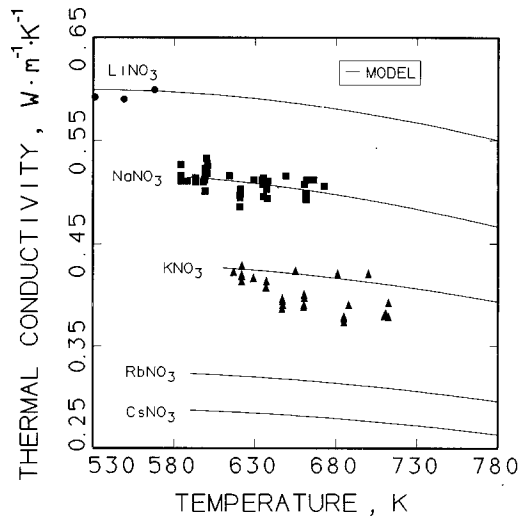


Fig. 8. Prediction of the thermal conductivity of the alkali nitrates from NaNO<sub>3</sub> data.

**Table III.** Model Performance for Sodium (1)–Potassium (2) Nitrate Mixtures

Composition (mol fraction NaNO <sub>3</sub> )	Claimed accuracy (%)	Avg. % dev.
0.0	±3–4	5.4
0.3	±3	6.3
0.46	±1	2.7
0.50	±3–4	3.5
0.75	±3	5.0
1.0	±3–4	1.5

The investigators (Nakazawa et al. [9]) reported that LiCl corroded the quartz container cell during the measurement so that the results have a larger uncertainty than the results for the other salts thus explaining the apparent discrepancy between the model and the data. In addition, the model may have a wider applicability than has been demonstrated in the present work. It may happen, for example, that the thermal conductivities of all the alkali halides may lie on the same curve as the alkali chlorides. Also, the model is easily extended to other classes of salts.

## 5. EXTENSION TO MIXTURES

Recent works on the thermal conductivity of molten sodium–potassium mixtures [26–28], have demonstrated that the thermal conductivity is a linear function of the mole fraction. The same is also approximately true for alkali halide mixtures [8]. Thus, the model can be easily extended to mixtures as follows:

$$\lambda = \sum_{i=1}^n x_i \lambda_i \quad (15)$$

where  $n$  is the number of components and  $x_i$  is the mole fraction of the  $i$ th component. The pure component thermal conductivity  $\lambda_i$  can be estimated as described in the previous sections. Tables III and IV show the results of

**Table IV.** Model Performance for Sodium (1)–Lithium (2) Nitrate Mixtures

Composition (mol fraction NaNO <sub>3</sub> )	Claimed accuracy (%)	Avg. % dev.
0.0	±3	1.0
0.5	±3	2.5
1.0	±3	1.5

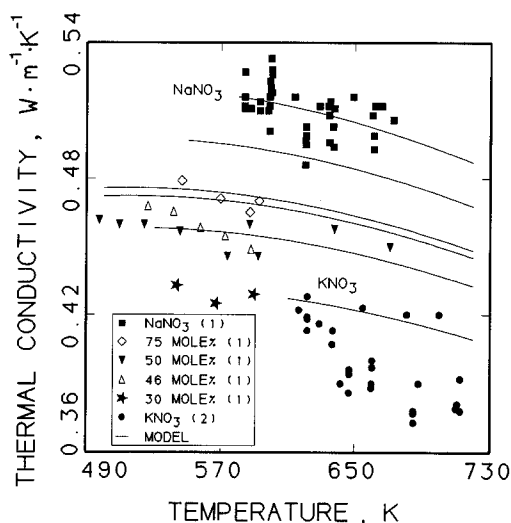


Fig. 9. Prediction of the thermal conductivity of nitrate mixtures from  $\text{NaNO}_3$  data.

using the linear mixing rule to estimate the thermal conductivities of binary nitrate mixtures from the fitted data for  $\text{NaNO}_3$  only. Figure 9 shows the sodium (1)–potassium (2) system results graphically. Although the data are reproduced within about 5%, all the predictions are higher than the data.

## 6. CONCLUSIONS

A model for the thermal conductivity of molten salts based on the rough hard-sphere theory was proposed. The model allowed the correlation of the thermal conductivity of families of compounds with a common anion. Given the behavior of a single member of a family of salts, the thermal conductivity can be predicted for the other members of the family. The model has a built-in density dependence and requires the molar volume of the molten salt and the solid salt at its melting point. The model was also found to work satisfactorily for mixtures of salts with a common anion.

## REFERENCES

1. Y. Nagasaka and A. Nagashima, *Int. J. Thermophys.* **12**:769 (1991).
2. R. M. DiGuilio, *The Thermal Conductivity of Molten Salts and Concentrated Aqueous Salt Solutions* (Ph.D. dissertation, Georgia Institute of Technology, Atlanta, 1991).
3. S. F. Y. Li, G. C. Maitland, and W. A. Wakeham, *High Temp. High Press* **17**:241 (1985).
4. A. Uhler, Jr., *J. Chem. Phys.* **20**:463 (1952).



5. J. Kestin and J. H. Whitelaw, *Trans. ASME* **88**:82 (1966).
6. V. D. Golyshev, M. A. Gonik, V. A. Petrov, and Y. M. Putilin, *Teplofiz. Vysokikh Temp.* **21**:899 (1983).
7. E. McLaughlin, *Chem. Rev.* **64**:389 (1964).
8. M. V. Smirnov, V. A. Khokhlov, and E. S. Filatov, *Electrochem. Acta* **32**:1019 (1987).
9. N. Nakazawa, Y. Nagasaka, and A. Nagashima, *High Temp. High Press.* (in press).
10. P. W. Bridgeman, *The Physics of High Pressures* (G. Bell and Sons, London, 1949).
11. J. F. Kincaid and H. Eyring, *J. Chem. Phys.* **6**:620 (1938).
12. A. G. Turnbull, *Aust. J. Appl. Sci.* **12**:324 (1961).
13. S. E. Gustafsson, N. O. Halling, and R. A. E. Kjellander, *Z. Naturforsch.* **23A**:682 (1968).
14. M. R. Rao, *Phys. Rev.* **59**:212 (1941).
15. M. R. Rao, *Indian J. Phys.* **16**:161 (1942).
16. Von F. A. Lindemann, *Phys. Zeitschrift* **11**:609 (1910).
17. J. K. Horrocks and E. McLaughlin, *Trans. Faraday Soc.* **59**:1709 (1963).
18. L. R. White and H. T. Davis, *J. Chem. Phys.* **47**:5433 (1967).
19. R. E. Young and J. P. O'Connell, *Ind. Eng. Chem. Fundam.* **10**:418 (1971).
20. Y. Tada, S. Hiroaka, T. Uemura, and M. Harada, *Ind. Eng. Chem. Res.* **27**:1042 (1988).
21. Y. Nagasaka and A. Nagashima, in *The Eleventh Japan Symposium on Thermophysical Properties* (Japan Society of Thermophysical Properties, Tokyo, 1990), pp. 275–278.
22. M. Harada, M. Tanigaki, and Y. Tada, *Ind. Eng. Chem. Fundam.* **22**:116 (1983).
23. S. F. Y. Li, R. D. Trengrove, W. A. Wakeham, and M. Zalaf, *Int. J. Thermophys.* **7**:273 (1986).
24. D. Chandler, *J. Chem. Phys.* **62**:1358 (1975).
25. S. Kitade, Y. Kobayashi, Y. Nagasaka, and A. Nagashima, *High Temp. High Press.* **21**:219 (1989).
26. T. Omotani, Y. Nagasaka, and A. Nagashima, *Int. J. Thermophys.* **3**:17 (1982).
27. T. Omotani and A. Nagashima, *J. Chem. Eng. Data* **29**:1 (1984).
28. R. Tufeu, J. P. Petitet, L. Denielou, and B. Le Neindre, *Int. J. Thermophys.* **6**:315 (1985).
29. G. J. Janz, *Molten Salts Handbook* (Academic Press, New York, 1967).
30. H. M. Roder, C. A. Nieto de Castro, and U. V. Mardolcar, *Int. J. Thermophys.* **8**:521 (1987).
31. Y. S. Touloukian, P. E. Liley, and S. C. Saxena (eds.), *Thermal Conductivity: Non-metallic Liquids and Gases, Vol. 3, The Thermophysical Properties Research Center Data Series* (Plenum Press, New York, 1970).
32. V. A. Rabinovich, A. A. Vasserman, V. I. Nedostup, and L. S. Veksler, *Thermophysical Properties of Neon, Argon, Krypton and Xenon* (Hemisphere, New York, 1988).
33. W. A. Wakeham, *High Temp. High Press.* **21**:249 (1989).