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The Thermal Conductivity of Molten $NaNO_3$ and KNO_3

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The thermal conductivity data for molten $NaNO_3$ and KNO_3 have been examined in order to propose recommended data sets for these two popular heat carriers and to establish the reference values above the temperature range covered by toluene and water. It is known that the measurement of the thermal conductivity of molten salts is very difficult, owing mainly to their corrosiveness and high melting temperatures, which introduce complications in apparatus design and significant systematic errors due to radiation and convection. However, some recent measurements seem to manifest more trustworthy values than obtained before. All available data have been collected and critically evaluated. The temperature range covered is 584 to 662 K for molten $NaNO_3$ and 662 to 712 K for molten KNO_3, with the confidence limits better than ±5%.

KEY WORDS: molten salts; potassium nitrate (KNO_3); sodium nitrate ($NaNO_3$); thermal conductivity.

1. INTRODUCTION

For the thermal conductivity of liquids the standard reference values are available in the temperature range from 190 to 370 K [1]. The standard reference materials recommended are toluene and water as the primary and *n*-heptane as the secondary. However, above this temperature range (>370 K), there are neither such internationally accepted values nor standard materials for liquid thermal conductivity. As far as the molten salts standard program [2] is concerned, reference values for the density, surface tension, electrical conductance, and viscosity of molten KNO_3 and NaCl have been recommended in the temperature range from 615 to

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1300 K. While reliable data for the thermal conductivity of molten salts are required in order to establish standard reference values, in practice there are only a few experimental studies whose discrepancies are often far beyond their claimed accuracy. This is due to the fact that measurement of the thermal conductivity of molten salts is difficult, owing mainly to their corrosiveness and high melting temperatures, which introduce complications in apparatus design and notable systematic errors due to radiation and convection. It is worthy to note that several measurements reported in the past have shown a large increase in the thermal conductivity of molten salts with increasing temperatures, which is not common for other normal liquids, with the exception of water. However, some recent measurements seem to manifest more trustworthy values of the thermal conductivity of molten salts. Consequently, it may now be possible to establish reference values as for the thermal conductivity of molten salts through critical evaluations of existing experimental studies, even though they are not so accurate as for toluene and water.

2. PROPOSED REFERENCE MATERIALS FOR LIQUID THERMAL CONDUCTIVITY AT HIGH TEMPERATURES

Janz [2] selected molten KNO_3 (melting point, 610.15 K) and NaCl (melting point, 1073.15 K) as reference materials for other properties for the following reasons. (1) These two salts are readily dried and are not strongly hydrated. (2) The melting points of these two salts span the temperature range for measurements with moderately high and high melting systems. (3) These two materials are available commercially in highest purities (99.999%) and at only moderate cost. McLaughlin [3] suggested that molten lead and molten $NaNO_3$ are appropriate as standard materials for liquid thermal conductivity above 300°C. Here, we propose $NaNO_3$ and KNO_3 as reference materials for the moderately high temperature range (about 580 to 740 K), since these two molten salts fulfill the criteria for standard materials [1] and those above-mentioned by Janz [2]. Moreover, for these two materials, several experimental studies with different techniques have been reported in comparison with other molten salts.

3. EVALUATION OF EXPERIMENTAL DATA

3.1. Assessment of Accuracy of Data

All existing experimental data are listed in Tables I and II. The general criteria are basically the same as described in Ref. 1. In addition to those,

Table I. Summary of Thermal Conductivity Measurements of Molten $NaNO_3$

Author(s)	Year	Method	Temperature range (K)	Purity (%)	Correlation	Claimed accuracy (%)	Data pts.	Grade
Turnbull [4, 5]	1961	Transient hot wire (without insulation)	582		—	±2.8	1	B
McLaughlin [3]	1964	Transient hot wire	586–738		—		13	B
Bloom et al. [7]	1965	Concentric cylinder (gap, 0.9 mm)	602–695	Reagent grade	—	±5	6	C
White and Davis [8]	1967	Concentric cylinder (gap, 3.18 mm)	613–693		$0.288_7 + 4.77_1 \cdot 10^{-4}\,T$	±3–±5	—	C
Gustafsson et al. [9, 10]	1968	Optical interferometry	588–727	Reagent grade	$0.2559 + 4.4 \cdot 10^{-4}\,T$	±2.6	9	C
McDonald and Davis [11]	1970	Concentric cylinder (gap, 2.54 mm)	583–733		$0.4023 + 2.6_8 \cdot 10^{-4}\,T$	±5	—	C
Omotani et al. [12]	1982	Transient hot wire (liquid metal probe)	588	99.9	—	±3	1	A
Santini et al. [13]	1984	Parallel plate	~583–~783		$0.28 + 5.0 \cdot 10^{-4}\,T$		—	C
Tufeu et al. [14]	1985	Concentric cylinder (gap, 0.2 mm)	593–673		—	±4	10	A
Kitade [16]	1989	Transient hot wire (ceramic-coated probe)	584–662	>99	$0.620_3 - 1._8 \cdot 10^{-4}\,T$	±3	28	A

Table II. Summary of Thermal Conductivity Measurements of Molten KNO_3

Author(s)	Year	Method	Temperature range (K)	Purity (%)	Correlation	Claimed accuracy (%)	Data pts.	Grade
Turnbull [4, 5]	1961	Transient hot wire (without insulation)	606		—	±2.8	1	B
Bloom et al. [7]	1965	Concentric cylinder (gap, 0.9 mm)	616–666	Reagent grade	—	±5	4	C
White and Davis [8]	1967	Concentric cylinder (gap, 3.18 mm)	613–703		$0.126_7 + 4.98_1 \cdot 10^{-4}\,T$	±3–±5	—	C
Gustafsson et al. [9, 10]	1968	Optical interferometry	611–724	Reagent grade	$0.4266 + 0.9 \cdot 10^{-4}\,T$	±2.6	8	C
McDonald and Davis [11]	1970	Concentric cylinder (gap, 2.54 mm)	613–733		$0.237_0 + 3.6_4 \cdot 10^{-4}\,T$	±5	—	C
Santini et al. [13]	1984	Parallel plate	~623–~773		$0.18 + 4.04 \cdot 10^{-4}\,T$		—	C
Tufeu et al. [14]	1985	Concentric cylinder (gap, 0.2 mm)	617–700		—	±4	5	A
Karasawa et al. [15]	1986	Transient hot wire (ceramic-coated probe)	623–663	99.9	—	±2	13	A
Kitade et al. [16]	1989	Transient hot wire (ceramic-coated probe)	622–712	>99	$0.627_5 – 3{.}_5 \cdot 10^{-4}\,T$	±3	22	A

because of the distinct difficulties associated with molten salts, the following factors were considered in making an assessment of accuracy:

(a) appropriateness of technique to high-temperature molten salts,
(b) possibility of radiative and convective heat losses,
(c) heat losses and any correction made,
(d) absolute or relative method,
(e) consistency of data, and
(f) purity and treatment of samples.

The reported thermal conductivity data have been classified into three grades based on the above-mentioned criteria.

Grade A: accurate within ±3 to ±4%.
Grade B: accurate within ±10 to ±15%.
Grade C: less accurate than ±15%.

3.2. Notes for Experimental Data

The following notes summarize the available experimental studies on the thermal conductivity of molten $NaNO_3$ and KNO_3. Emphasis is placed on the appropriateness of the techniques used under high-temperature conditions. It should be noted that all these measurements were carried out under atmospheric pressure.

(1) Turnbull [4, 5]. A transient hot-wire apparatus was employed without insulation on the wire. A bare 50-μm-diameter platinum wire (length, 100 mm) was used as a hot wire. Thick copper leads were insulated by glass tubes. A single measurement lasted 1 min, which seems too long to achieve proper thermal conductivity measurements by this method, especially under high-temperature conditions. The maximum claimed error was ±2.8%. For pure $NaNO_3$ and KNO_3, only one result near melting point has been tabulated [5]. Although Turnbull concluded that the electrical conductivity of salts was negligible under the experimental conditions, the data obtained by the same method for HTS (KNO_3–$NaNO_3$–$NaNO_2$, 44–7–49 mol%) show serious electrical conductivity effects as pointed out by Omotani et al. [6].

(2) McLaughlin [3]. McLaughlin recommended molten $NaNO_3$ as a reference standard material for the thermal conductivity of liquids above 300°C. The author provisionally recommended his own values obtained by the transient hot-wire method in the temperature range from 300 to 460°C (573 to 733 K). However, details of the apparatus and the procedures are

unknown. It is plausible that appropriate hot-wire insulation techniques did not exist at that time. Therefore, their data might be affected substantially by the leakage current through electrically conducting molten salt.

(3) Bloom et al. [7]. A concentric-cylinder apparatus was used. The cylinders were made of about a 120-mm length of silver and the gap between two cylinders was 0.9 mm. Thermocouples of 13% rhodium–platinum were used for temperature measurement. All salts used were of analytical reagent grade. The reproducibility was ±5% and the accuracy was claimed to be ±5%. No correction for radiation was made due to the low emissivity of silver and the small annulus thickness. The data show a strong positive temperature dependence for both $NaNO_3$ and KNO_3.

(4) White and Davis [8]. A concentric-cylinder apparatus was used with a thickness of the fluid layer of 3.18 mm and a temperature difference of less than 1°C. Conduction heat losses were applied amounting to 20 to 33% of the total heat supplied. But no detailed description on this point was presented in the paper. No correction was applied for radiation owing to the strong infrared absorption coefficient of the samples. The claimed accuracy was ±3 to ±5%. Only correlations of the measured data are available. It should also be noted that they discussed the positive temperature dependence of their own thermal conductivity results in some detail and they criticized the use of the transient hot-wire method applied to molten salts by Turnbull [4].

(5) Gustafsson et al. [9, 10]. They measured the thermal conductivity and the thermal diffusivity of molten $NaNO_3$ and KNO_3 with the aid of a non-steady-state optical interferometric technique (plane source technique). The plane source was realized by using an electrically heated metal foil suspended in the liquid. The temperature distribution is described by using the concept of instantaneous heat sources giving a simple expression of the optical path, which is recorded with wave-front-shearing interferometry. The approximate dimensions of the used foils were $0.009 \times 32 \times 86\ \text{mm}^3$ silver for KNO_3 and $0.010 \times 40 \times 86\ \text{mm}^3$ platinum for $NaNO_3$. The measurements were completed within 10 s. Error due to radiation was considered to be negligible. The accuracy was claimed to be ±2.6% for the thermal conductivity and ±3% for the thermal diffusivity. The investigators did not consider the effect of current leak from the bare metallic metal foil heat source to molten salt.

(6) McDonald and Davis [11]. A concentric-cylinder apparatus (silver cylinder) was used. The gap holding the molten salt between the cylinders was 2.54 mm and the length of the inner cylinder was 177.8 mm. The apparatus was operated in an relative mode calibrated against ethylene

glycol and Dowtherm. Only correlations are available. There are no descriptions concerning the purity of samples and accuracy. It should be noted that this study is a remeasurement of the same molten salts with a similar (or may be modified) apparatus by the same group [8]. The remeasurement seems to be conducted because the previous results were considered to be in error due to heat losses and convection. This might be the reason why they mentioned a supramica insulating cap to reduce heat losses and why they reduced the gap from 3.18 mm to 2.54 mm. The temperature coefficients of the thermal conductivity became smaller for both materials. But even so, their results still seem to be inconsistent, because for $NaNO_3$ the remeasurement gave smaller values, but for KNO_3 the situation is reverse. For these reasons, the data reported by this group [8, 11] are judged to be not good enough for reference values.

(7) Omotani et al. [12]. The method applied was a modified transient hot-wire method with liquid metal (mercury) in a capillary as a heat source. The capillary is made of quartz glass with an outer diameter of about 90 μm and an inner diameter of 45 μm. The length of the capillary is about 100 mm. The apparatus was operated in a relative mode calibrated against toluene. The accuracy of the measurement is claimed to be $\pm 3\%$. They succeeded to eliminate errors due to convection.

(8) Santini et al. [13]. The principle of the measurement is the relative parallel-plate method with heat flowing downward. The heat flux was measured by a "fluxmeter" under which there exist thermal bond material and molten salt. The standard of thermal conductivity used for calibration was silicone oil. No descriptions concerning the gap, raw data, purity, and temperature range for the correlations were presented. This sort of steady-state method is suited only for solid materials. The application of this method to liquids, especially to high-temperature molten salts, inevitably introduces considerable systematic errors due to convection and heat losses.

(9) Tufeu et al. [14]. The measurement was performed with the concentric-cylinder method. The gap filled with the salt was 0.2 mm and the length of the cylinder was 120 mm. Silver was used as the cylinder material. The surfaces limiting the sample were polished and their emissivity was estimated to be 0.02. The temperature difference between the cylinders was adjusted to about 1.5°C. The accuracy of the measurement was estimated to be better than $\pm 4\%$. They concluded that the thermal conductivity of these molten salts is temperature independent.

(10) Karasawa et al. [15]. The principle of the measurement was based on the absolute transient hot-wire method with a ceramic-coated

probe. After many trials of insulating the probe, the most suitable probe was found to be a platinum thin wire coated with SiO_2 prepared by a metal alkoxide hydrolysis process and titanium leads insulated by plasma sprayed Al_2O_3 with SiO_2 upper coating. The usefulness of the probe was tested by measuring the thermal conductivity of molten KNO_3 in the temperature range from 623 to 663 K. The accuracy was claimed to be ±2%.

(11) Kitade et al. [16]. Absolute transient hot-wire method with ceramic-coated probes was used. The probe was a modified version of that described in Ref. 15 by the same research group. The hot wire was a 30-μm-diameter platinum with four-terminal-type construction. The platinum wire was insulated by Al_2O_3 produced with the aid of ion plating (about 4-μm thickness). Titanium leads were coated with plasma-sprayed Al_2O_3. In order to fill small pores in the sprayed layer, Si–Ti–C–O ceramic paint was used as an extra protective layer. Five different probes were used to cover the entire range of measurements. The accuracy was claimed to be ±3%. Results obtained from different probes agreed well with each other within the estimated accuracy.

3.3. Primary Data and Recommended Correlations

3.3.1. $NaNO_3$

Figure 1 shows all available experimental data and correlations for the thermal conductivity of molten $NaNO_3$. (Melting point is 580.15 ± 1 K and the melt is stable in air to approximately 773 K; at higher temperatures, the melts decomposes to form $NaNO_2$ and oxygen [17].) As indicated in Table I, the primary data selected are those of Omotani et al. [12] (transient hot wire with liquid metal probe), Tufeu et al. [14] (concentric cylinder), and Kitade et al. [16] (transient hot wire with ceramic-coated probe). At the present time, we recommend the correlation proposed by Kitade et al. [16].

$$\lambda = 0.620_3 - 1._8 \times 10^{-4}\,T, \qquad 584 < T < 662\ \mathrm{K} \tag{1}$$

where λ is in $W \cdot m^{-1} \cdot K^{-1}$ and T is in K. Although the accuracy of the determination of the thermal conductivity as a function of temperature is slightly poor, the temperature dependence of the thermal conductivity is not positive as assumed previously but it is weakly negative. Figure 2 shows the deviations of the existing experimental data from Eq. (1). As can be seen, the primary data agree with Eq. (1) within about ±5%, which would be the accuracy of the present recommendation. The deviations of the existing correlations from Eq. (1) are shown in Fig. 3. The recommended values of Janz et al. [17], which are based on the correlation of

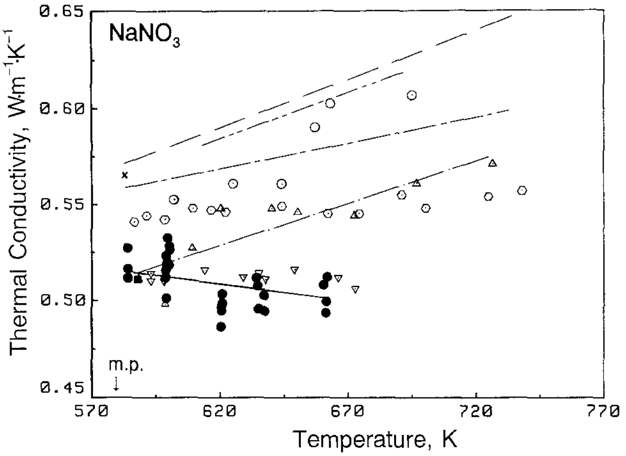

Fig. 1. The thermal conductivity of molten NaNO$_3$. Symbols for Figs. 1 to 6: ×, Turnbull [4, 5]; ⊙, McLaughlin [3]; ⊙, Bloom et al. [7]; △, Gustafsson et al. [9, 10]; ■, Omotani et al. [12]; ▽, Tufeu et al. [14]; ⊡, Karasawa et al. [15]; ●, Kitade et al. [16]; ——-——, White and Davis [8]; —-—, McDonald and Davis [11]; - - -, Santini et al. [13]; ——·——, Gustafsson et al. [9, 10]; ——, Kitade et al. [16].

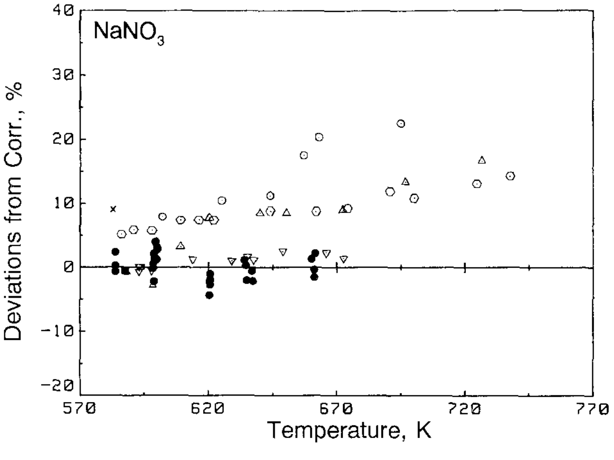

Fig. 2. The deviations of the available experimental data for the thermal conductivity of molten NaNO$_3$ from the correlation of Eq. (1). Symbols are the same as in Fig. 1.

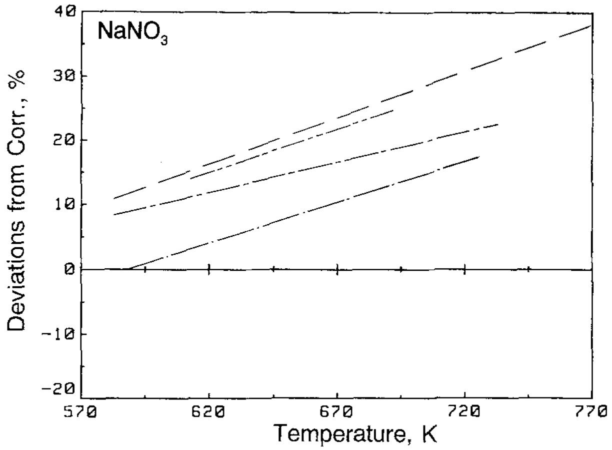

Fig. 3. The deviations of the other correlations for the thermal conductivity of molten NaNO$_3$ from the correlation of Eq. (1). Symbols are the same as in Fig. 1.

McDonald and Davis [11], differ by 20% from the present recommendation. Table III gives recommended values for the thermal conductivity of molten NaNO$_3$ at atmospheric pressure calculated from Eq. (1).

3.3.2. KNO$_3$

Figure 4 shows all available experimental data and correlations for the thermal conductivity of molten KNO$_3$. (Melting point is 610.15 ± 1 K and

Table III. Recommended Thermal Conductivities for Molten NaNO$_3$

Temperature T(K)	Thermal conductivity λ (W·m^{-1}·K^{-1})
590.0	0.514
600.0	0.512
610.0	0.511
620.0	0.509
630.0	0.507
640.0	0.505
650.0	0.503
660.0	0.502
670.0	0.500
680.0	0.498
690.0	0.496
700.0	0.494
710.0	0.493
720.0	0.491

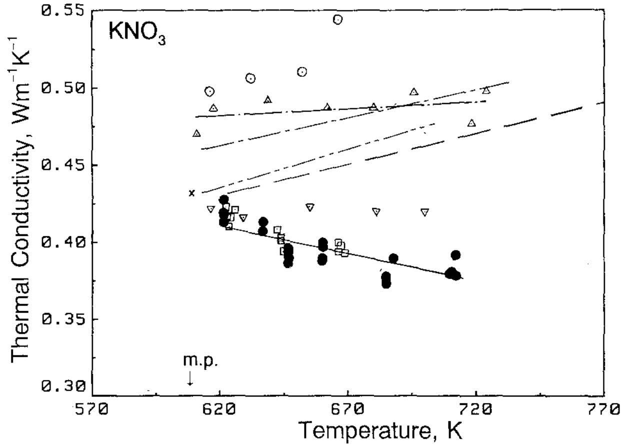

Fig. 4. The thermal conductivity of molten KNO_3. Symbols are the same as in Fig. 1.

KNO_3 melts without decomposition to a liquid which is stable in air at least to approximately 803 K [17].)

As indicated in Table II, the primary data selected are those of Tufeu et al. [14] (concentric cylinder), Karasawa et al. [15] (transient hot wire with ceramic-coated probe), and Kitade et al. [16] (transient hot wire with ceramic-coated probe). At the present time, we recommend the correlation proposed by Kitade et al. [16].

$$\lambda = 0.627_5 - 3._5 \times 10^{-4}\, T, \qquad 622 < T < 712\ \mathrm{K} \tag{2}$$

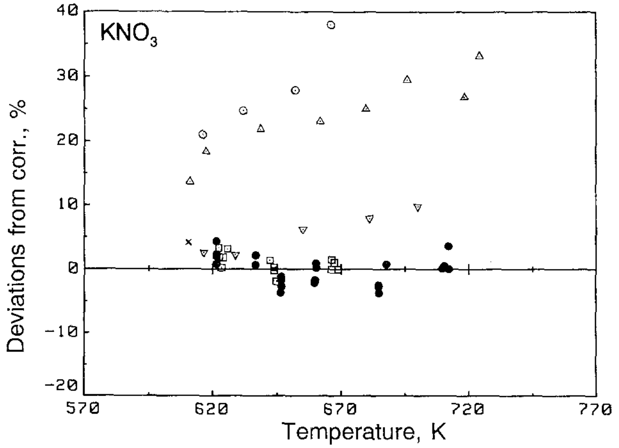

Fig. 5. The deviations of the available experimental data for the thermal conductivity of molten KNO_3 from the correlation of Eq. (2). Symbols are the same as in Fig. 1.

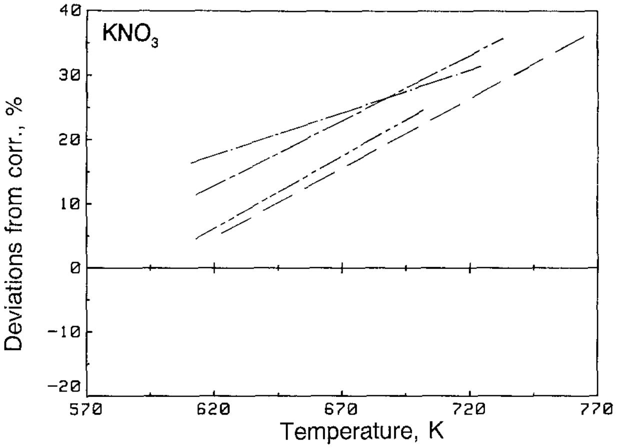

Fig. 6. The deviations of the other correlations for the thermal conductivity of molten KNO_3 from the correlation of Eq. (2). Symbols are the same as in Fig. 1.

where λ is in $W \cdot m^{-1} \cdot K^{-1}$ and T is in K. Figure 5 shows the deviations of existing experimental data from Eq. (2). As can be seen, the data of Karasawa et al. [15] and Kitade et al. [16] agree with Eq. (2) within about ±5%, which would be the accuracy of the present recommendation. However, the results of Tufeu et al. [14] differ by +10% at the highest temperature even though the agreement near the melting point is quite reasonable. The deviations of the existing correlations from Eq. (2) are shown in Fig. 6. The recommended values of Janz et al. [17], which are

Table IV. Recommended Thermal Conductivities for Molten KNO_3

Temperature T(K)	Thermal conductivity $\lambda\,(W \cdot m^{-1} \cdot K^{-1})$
620.0	0.411
630.0	0.407
640.0	0.404
650.0	0.400
660.0	0.397
670.0	0.393
680.0	0.390
690.0	0.386
700.0	0.383
710.0	0.379
720.0	0.376

based on the correlation of McDonald and Davis [11], differ by more than 30% from the present recommendation. Table IV gives recommended values for the thermal conductivity of molten KNO_3 at atmospheric pressure calculated from Eq. (2).

4. CONCLUSIONS

It is concluded that the older experimental data for $NaNO_3$ and KNO_3, measured mainly by the steady-state methods, contain significant systematic errors due to radiation and convection. Especially, the recommended values for these molten salts by NSRDS [17], which are based on the data of McDonald and Davis [11], differ by 20 to 30% at most from the present recommendations. As a consequence, it is necessary to reassess these recommendations for the thermal conductivity of molten salts.

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