Determination of the Thermal Conductivities of Several Molten Alkali Halides by Means of a Sheathed Hot-Wire Technique

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Abstract—A modification of the transient hot-wire method has been used for the measurement of the thermal conductivities of electrically conducting fluids. Although the method is probably not as accurate as the concentric-cylinder method in similar applications, it avoids radiation problems which hamper studies with many molten salts. We report here hot-wire measurements of the thermal conductivity values for molten alkali halides. These results indicate that, as was noted by White and Davis[1] for alkali nitrates, the temperature dependence of the thermal conductivities for those substances is positive. Such a temperature dependence seems to be an intrinsic property of ionic liquids and is not associated with the internal degrees of freedom of the ions constituting a molten salt.

1. Introduction

We report here a version of the transient hot-wire method modified by quartz sheathing for use in measuring thermal conductivities of electrically conducting fluids. Experimental results for several alkali halides are discussed.

The thermal conductivity of molten salts has only recently begun to be studied in a systematic manner. A review of methods used for the determination of the thermal conductivity of fluids is given by Tsederburg.[2] Filippov[3] has discussed several recently developed

relative methods, some of which can measure the thermal conduc-
tivity of very small quantities of liquids. In Table 1 we have listed
some thermal conductivity experiments reported in the literature for
pure and binary mixtures of molten salts, including the substances
studied and the type of apparatus used.

TABLE 1   Experiments Performed to Determine the
Thermal Conductivity of Molten Salts

Author	Year	Type of apparatus	Substances studied
Lucks and Deem[5]	1956	Horizontal-layer	NaOH
Turnbull[6]	1961	Hot-wire	$NaHSO_4$, $KHSO_4$, KNO_3, $KCNS$, NH_4HSO_4, $AgNO_3$, $ZnCl_2$
Bloom[7]	1965	Concentric-cylinder	$NaNO_3$, KNO_3, $AgNO_3$, $NaNO_2$, $(Na—K)NO_3$, $(Ag—Na)NO_3$, $(Ag—K)NO_3$
White and Davis[1]	1967	Concentric-cylinder	$LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, $CsNO_3$
Gustafsson et al.[4]	1967	Optical plane source	$LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, $CsNO_3$
Cornwell and Dyson[8]	1969	Hot-wire	$ZnCl_2$, $AgCl—AgI$ eutectic
McDonald and Davis[9]	1970	Concentric-cylinder	$LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, $CsNO_3$, $(Li—Cs)NO_3$, $(Na—K)NO_3$, $(Na—Cs)NO_3$, $(K—Rb)NO_3$, $(Rb—Cs)NO_3$,

An advantage of the horizontal-layer method is the possibility of
easy replacement of parts if corrosion is occurring, but a disadvantage
is the inherent presence of a large heat leakage. Methods used to
reduce this end-effect have a limited accuracy. In this case a relative
method involves a simpler apparatus and the measurements require
less time.

The concentric-cylinder method is often used and can be designed

to have a low end-effect with a resulting fair accuracy, but as in the case of the horizontal-layer method the collection of data can be a slow procedure. This is mainly due to the greater time required for the establishment of thermal equilibrium during the steady-state reading.

An optical method used by Gustaffson et al.[4] involving interferometry studies in a liquid containing a heated metal foil, appears to give good reproducibility of results with fair accuracy and is quite rapid.

Thermal radiation is an important source of error. It can be made insignificant in the hot-wire method and also in Gustaffson's optical (hot-foil) method, but in the concentric-cylinder and similar methods it may cause a significant error depending on the properties of the fluid and the nature of the metallic surfaces. Based on the observations of Janz and James,[10] the radiation effects in alkali nitrates have been assumed to be negligible by recent experimenters using the concentric-cylinder method (Bloom,[7] White and Davis,[1] McDonald and Davis[9]). However the radiation effect with molten alkali halides is probably more serious, due to the higher temperature of melting as well as the well-known greater transparency of these salts to infra-red radiation as witnessed by their use as windows and pellets in infrared spectroscopy. In the face of such uncertainty an experimental method wherein the radiation effect is known to be small is much to be preferred.

An additional error is introduced if electrically conducting fluids are to be studied. The hot-wire apparatus permits the passage of an electric current through the salt. Turnbull[6] argued that this effect is small but White and Davis[1] using a similar technique found that the resulting error is large enough to make the method inapplicable to molten salts. White[11] has discussed how the effect of electrical conduction in the fluid can be observed and we shall discuss this phenomenon below.

To employ the hot-wire technique we have developed a method of electrically insulating the fluid from the wire. Our findings support those of White. In using their optical apparatus Gustaffson et al. have assumed that if the voltage drop across a hot-foil is below the decomposition voltage of the salt that the error due to current flow and heating in the salt is negligible.

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2. Experimental Technique

A. WORKING FORMULA FOR THE HOT-WIRE METHOD

Carslaw and Jaeger[12] give the mathematical basis of the hot-wire method. Suppose that a fine wire made of a perfect conductor is immersed in an infinite medium whose initial temperature is T_0, and is heated at the rate Q per unit length per unit time for $t > 0$. For times other than those which are very small the temperature T of the wire at time t is given by

$$T - T_0 = \frac{Q}{4\pi\kappa}\left[2h + \ln\frac{4\tau}{C} - \frac{(4h - \alpha_1)}{2\alpha_1\tau} + \frac{\alpha_1 - 2}{2\alpha_1\tau}\ln\frac{4\tau}{C} + \ldots \right] \tag{1}$$

where

$$h = 2\pi R\kappa$$
$$\alpha_1 = 2\pi a^2 \rho C/S_1$$
$$a = \text{radius of the conductor}$$
$$\tau = Kt/a^2$$
$$\kappa = \text{thermal conductivity of the medium}$$
$$\rho = \text{density of the medium}$$
$$K = \text{thermal diffusivity of the medium}$$
$$R = \text{thermal resistance per unit length of conductor}$$
$$S_1 = \text{thermal capacity of wire}$$
$$C = 1.781$$

We see that for sufficiently large values of time, $T - T_0$ has a linear asymptote equal to $\ln t$. The experimental problem is clear, one must measure the temperature rise of the wire as a function of time when it is heated with constant power. The linear portion of a plot of $T - T_0$ vs $\ln t$ has the slope $Q/4\pi\kappa$ from which κ is determined directly.

B. PROBE AND ELECTRICAL CIRCUITRY

Turnbull[6] used the hot-wire method to measure thermal conductivities of several different pure molten salts and mixtures of molten salts. His results however were not all consistent, and there is now evidence that an error due to current loss through the salt was inherent to Turnbull's method. In fact White[11] constructed a probe similar to the one Turnbull used and demonstrated that, although the probe gave accurate results for water, it gave incon-

sistent results for molten salts, presumably because of the current flow through the salt.

We have overcome the problem of Turnbull's original probe (and White's) by insulating the hot-wire with quartz. Our probe is shown in Fig. 1.

Heavy (22 gauge) platinum lead-in wires were strung through the quartz tubing. The finer wire, 0.004 in. diameter platinum, was welded to the heavier leads using a Unitek Weldmatic Capacitative Arc Welder.

It should be noted that the thermal resistance of air lying between
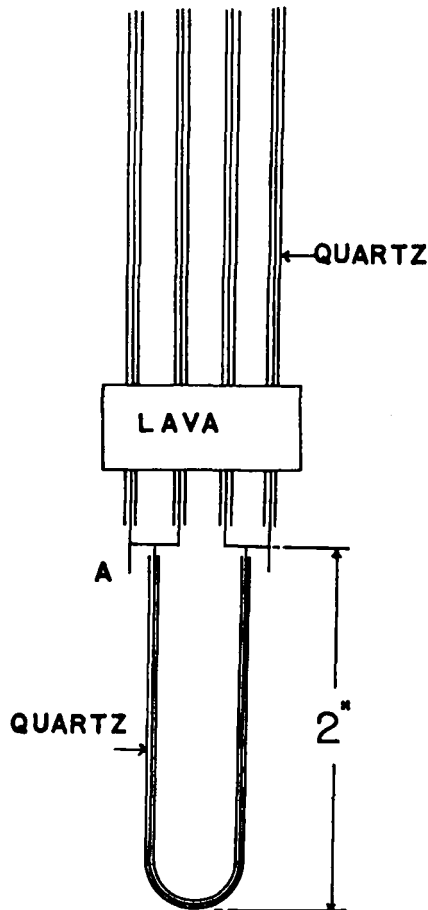
Figure 1. Probe used in this work.

the wire and the quartz is not of great importance even if it is of the same order of magnitude as that of the quartz, because its thermal capacity is small.

Figure 2 is a schematic diagram of the bridge circuit used in the measurements. The fine wire plus a precision one Ω resistor, R_p, made up one arm of the bridge. The other bridge arms consisted of General Radio Corp. decade resistors. Power was supplied by a Sorenson D.C. power supply.

The bridge circuit is a conventional resistance thermometer circuit; however for our experiment its transient behavior was of interest. Experimentally, we needed a curve of $T - T_0$ vs time.

Figure 2. Bridge circuit for hot-wire probe.

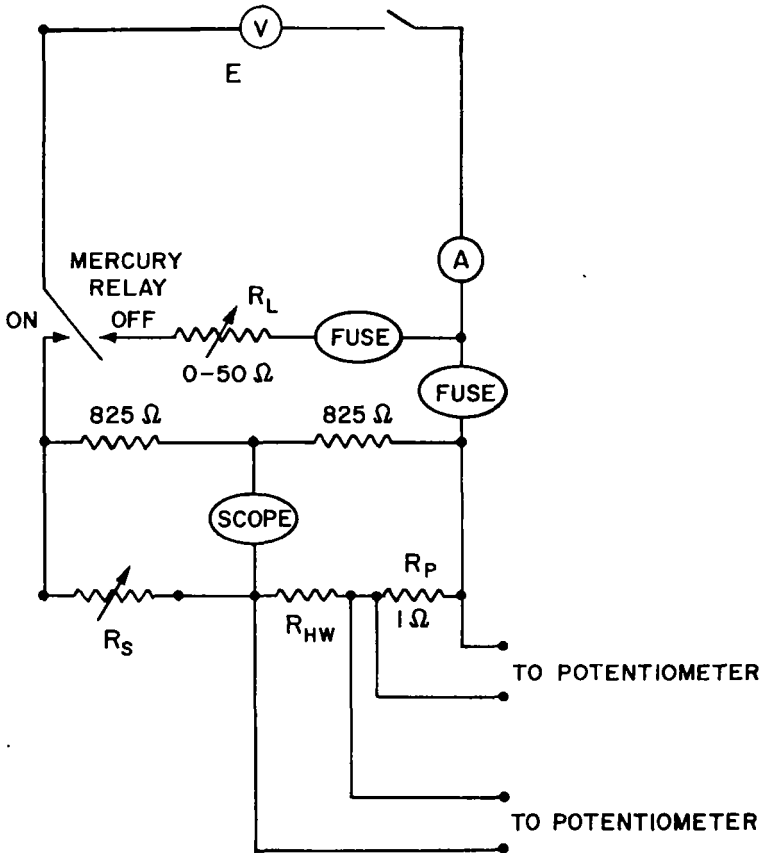Since the resistance of the wire can be calibrated against temperature by steady-state measurements it sufficed to determine the resistance change of the wire after the heating current was switched to it. Let ΔR be the change in resistance of the wire upon heating and ΔE the change of voltage observed by the oscilloscope. Let $A^{\cdot}$ be the ratio of $R_P + R_S + R_{HW}$ to R_S. If A equals 2 then the following relationship holds for any value of line resistance.

$$\frac{\Delta E}{\Delta R} = \frac{I}{2} \tag{2}$$

C. The Resistance Thermometer

In 1887 Callendar[14] introduced a formula for estimating temperature through the use of a platinum resistance thermometer:

$$T = \frac{R - R_0}{R_{100} - R_0} \, 100 + \zeta \left(\frac{T}{100} - 1 \right) \frac{T}{100} \tag{3}$$

R_0 and R_{100} are the resistances of the platinum wire at 0 °C and 100 °C, ζ is a constant characteristic of the individual thermometer. Heycock and Neville[15] tested the formula to 1000 °C.

Differentiating Eq. (3) gives

$$\frac{\mathrm{d}T}{\mathrm{d}R} = \frac{100}{R_{100} - R_0} \left[1 - \zeta \left(\frac{2T}{100^2} - \frac{1}{100} \right) \right]^{-1}. \tag{4}$$

From the theory of the hot-wire method already discussed we have

$$\Delta T = \frac{Q}{4\pi\kappa} \cdot \Delta \ln t. \tag{5}$$

Approximately

$$\Delta T = \Delta R \times \frac{\mathrm{d}T}{\mathrm{d}R} = \Delta E \times \frac{2}{I} \times \frac{\mathrm{d}T}{\mathrm{d}R} \tag{6}$$

or

$$\kappa = 0.0398 \, \frac{Q \, I \, \Delta \ln t}{\Delta E \times (\mathrm{d}T/\mathrm{d}R)} \tag{7}$$

$$Q = \text{power/cm.} = \frac{I^2 r}{4.187} \tag{8}$$

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where I is the current in amps, r is the resistance per unit length in ohms/cm.

We finally get the working formula

$$\kappa = \frac{9.50 \times 10^{-3} \, r \, I^3 \, \varDelta \ln t}{(dT'/dR) \, \varDelta E} \text{ cals./cm. sec. °C} \tag{9}$$

D. Furnace Design

A constant-temperature furnace capable of providing steady temperatures up to 950 °C was constructed and is shown schematically in Fig 3.

A massive block of nickel was used to provide a thermostat. Chromel-alumel thermocouples inserted in this block were used as sensing elements for the controller. An API Instruments Co. controller (Cat. No. 916–B Control-Pak and two model 603–L optical meter relays, 0–500 °C and 500–1100 °C) was used to control the temperature.

Test liquids were contained in a long quartz or Vicor tube. These tubes will withstand continuous service at up to 950 °C in the case of Vicor and higher for quartz. It is worthwhile noting that if a molten salt is allowed to solidify in a Vicor tube and then cooled it will crush the tube. It was necessary to prepare pipets of Vicor and to use these to withdraw the salt. Further details of experimental design and technique are available.[13]

E. The Problem of Polarization

In the case of molten salts the medium surrounding the wire is a conductor and a considerable fraction of the total current may be flowing through the melt immediately after the step pulse of power is applied. This physical problem has been analyzed by Smythe,[16] who gives the following equation for the ratio of the resistance of the wire immersed in an infinite bath of conducting liquid to the resistance of the wire alone:

$$\frac{R_1}{R_2} = 1 + \frac{8C \, \tau_1}{\pi^2 \, a \, \tau_2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \frac{K_1[(2n+1)\pi \, a/C]}{K_0[(2n+1)\pi \, a/C]} \tag{10}$$

where τ_1 = resistivity of the wire

$\quad a$ = radius of the wire

$\quad C$ = length of the wire

$\quad \tau_2$ = resistivity of the medium

$\quad K_j$ = jth order modified Bessel function of the 2nd kind

$\quad R_1$ = resistance of wire alone

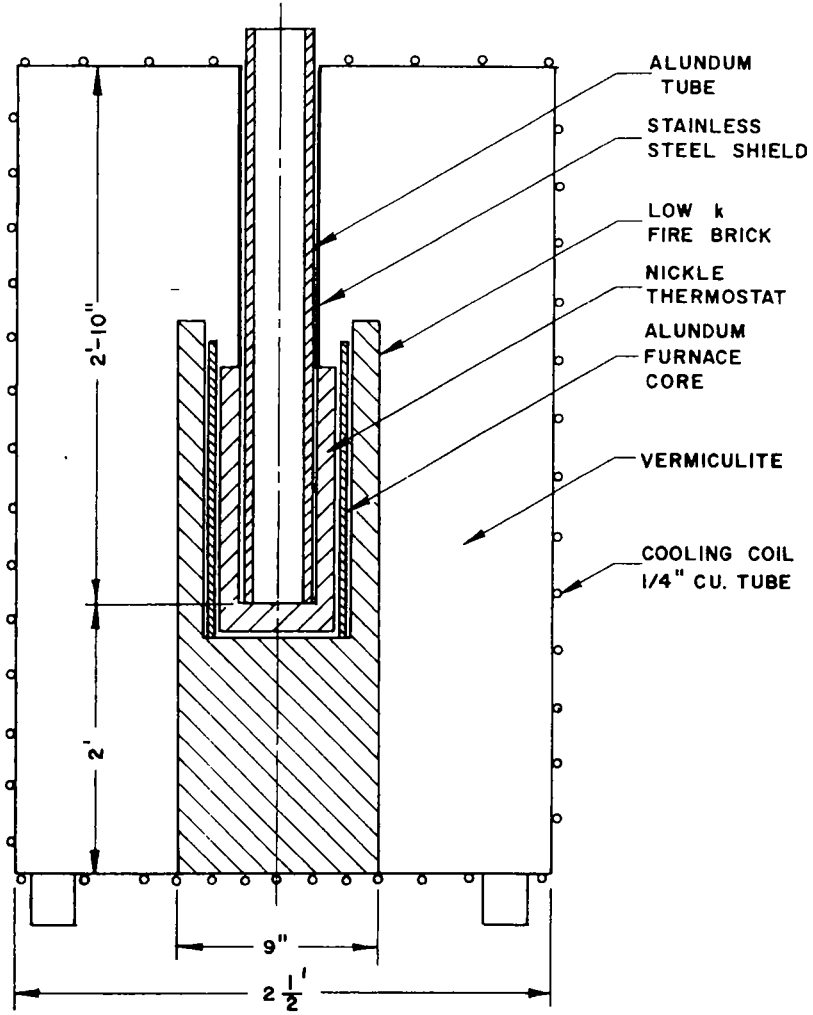$\quad R_2$ = resistance of wire-melt system

Figure 3. Furnace design.

For a wire of radius 0.025 cm and length 2 cm about 20% of the current can pass through the salt. The steady passage of ions through the salt carrying the current will continue only if the voltage drop along the wire is above the decomposition voltage of the salt, so that electrolysis is occurring at the wire-salt interface. According to Eq. (10) reducing the ratio C/a should decrease the error but it is found in practice that the resulting loss of transient response of the hot-wire on application of the heating current makes a compromise impracticable if reasonably accurate results are desired. Turnbull used a heating wire and current similar to those used by White and Davis (length 10 cm, radius 0.025 cm, current 200–300 m amps). The validity of Turnbull's findings and method is therefore in serious doubt as are the findings of Cornwell and Dyson who used Turnbull's method.

Now the change in resistance of the wire is reflected in a change in voltage across the bridge and is portrayed as a transient on a C.R.O. screen.

If the effect of heating the wire and causing an increase in resistance is to produce a positive transient on the screen then the effect of current leakage through the salt is to produce a large negative display even if the resistance of the wire has not had time to change significantly. This is particularly important since the C.R.O. is acting as a null-detector. The polarization transition time for molten salts is of the order of one second[17] and the resulting calculated value of thermal conductivity will be too small. This problem is satisfactorily solved by means of quartz insulation around the wire.

F. DESCRIPTION OF A TYPICAL RUN

The probe is lowered slowly into the Vicor tube until it is about 1–2 inches above its final level. From here the probe is lowered slowly by means of a fine adjustment in the form of a screw-threaded bolt. With reference to Fig 2, R_s is adjusted until the bridge is approximately balanced. The D.C. power supply is set to about 10 V. The traces on the screen of the C.R.O. obtained by switching the power to the hot-wire on and off are observed on the screen. Adjusting R_s enables the traces to be observed consecutively in approximately the same position on the screen for convenience.

If the wire is unbroken and no salt is inside the thin quartz in-

sulator, the curve protrayed on the screen on switching on the power is asymptotic and exponential. The curve portrayed on switching off the power should be a horizontal line except for perhaps the first hundredth of a second or so. This situation is shown in Fig 4A where the upper trace represents the switching on of the step voltage and the lower trace represents the switching off. The probe is lowered a turn at a time and the power switched on and off. The procedure is repeated until the signals on the screen change position abruptly. The decay signal becomes exponential usually covering several millivolts on the screen. This situation is shown in Fig 4B. This means that the two extensions of the platinum leads A are both touching the salt. The probe is now raised half a turn at a time until once more the decay signal is horizontal. The probe is now correctly positioned. The power supply is set to about 10 V, the trace on the screen adjusted and a photograph taken. From the equations already discussed the value of thermal conductivity of the salt can be calculated apart from a calibration factor.

The calibration factor is made necessary by the presence of the quartz surrounding the hot-wire but only involves a correction of about 15%. The calibration factor can be calculated by making use of a fluid whose thermal conductivity is well known. This is true for water at 0 °C and for molten alkali nitrates. We used sodium nitrate over a temperature range of 100 °C and found no temperature dependence of the calibration factor. In addition this factor was identical to within 1–2% of that obtained using water at its freezing point. Having ascertained these facts, the wires used subsequently were calibrated with water at 0 °C.

G. Errors in the Hot-Wire Method

An important potential source of error is thermal convection. However this is easily tested. If convection does not occur then a plot of ΔE versus ln t yields a straight line, where ΔE is the voltage read on the C.R.O. with an arbitrary datum level, and t is the time in arbitrary units (the horizontal deflection on the screen can be used without reference to the time scale). Another source of error stems from the frequent replacement of wires and quartz due to corrosion and breakage and the resulting necessary recalibration. A frequent cause of breakage of the quartz wire insulator is probably the tend-
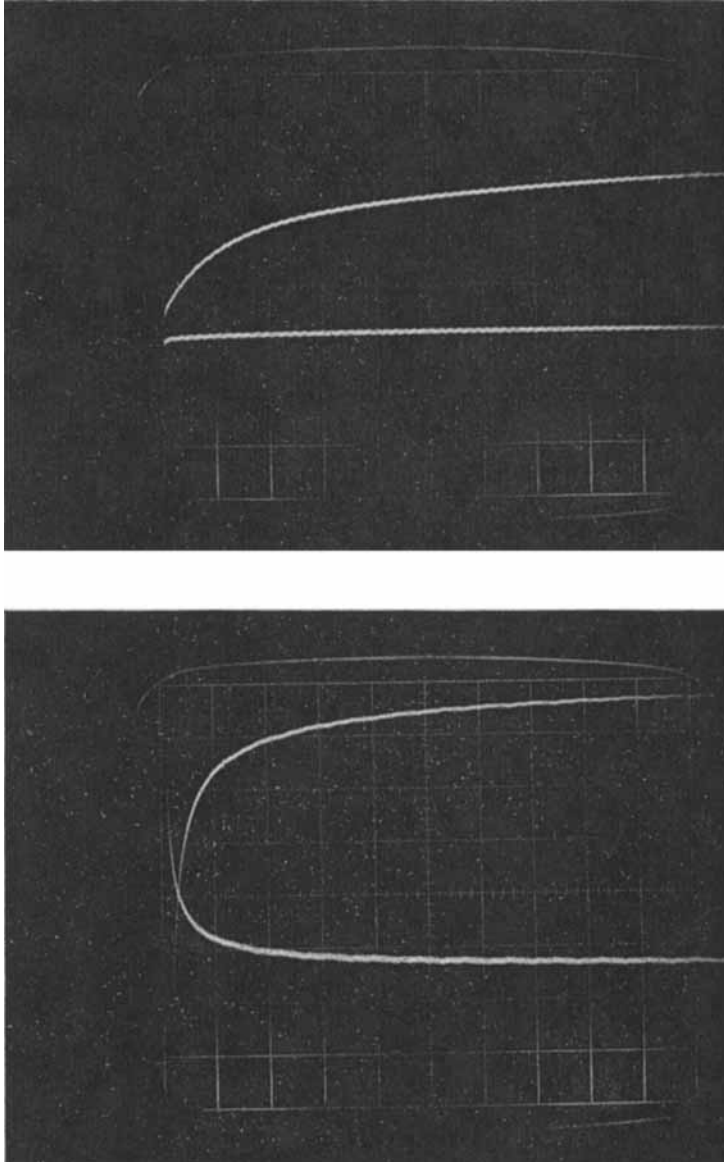
Figure 4. A. (upper) Switch-on and switch-off C.R.O. traces with no polarization.
B. Corresponding traces with polarization.

ency of the salt when freezing and contracting to damage the former to which a small amount of salt will adhere when the probe is removed from the melt. This is unavoidable if the probe must be removed from the furnace when changing salts but during the process of changing the temperature of a given salt the probe should be kept near the surface of the melt. Pyrex may be used instead of quartz if alkali nitrates are to be studied at lower temperatures. Also no two probes are geometrically identical. The water calibration is performed with the wire completely immersed, unlike an actual run with a salt. Repeated runs at a given temperature with several salts yield experimental data with a reproducibility spread of 5% using the same hot wire. An estimate of the maximum likely error in the values of thermal conductivity is 10%. Most of this possible error would appear in the differences between the values for two salts rather than in values for one salt at more than one temperature. The observed temperature dependence of thermal conductivity is subject to a larger error due to its smaller value.

H. CORROSION PROBLEMS

Corrosion of the Vicor tube in which the salt is placed is severe due to the presence of the salt. Most of the corrosion occurs a few inches above the level of the salt. A likely explanation is that metal atoms are deposited here and are more corrosive than the metal ions present in the salt. Certainly traces of iodine vapor can be detected coming from the top of the furnace if the latter is opened while an iodide salt is being studied. The resulting corrosion will eat through the tube within a few days and cause it to disintegrate. Corrosion of the inconel support bars also occurs but is at an acceptable level.

3. Discussion of Results

The results obtained are listed in Table 2. In the case of the pure alkali nitrate melts the thermal conductivity increases mono-tomically with a decrease in the atomic weight of the metallic cation. The results in Table 2 appear to be self consistent in that an increase of either cationic or anionic weight with the other held constant leads to a decrease in thermal conductivity. This characteristic appears to be a property of most chemical homologous series, and is

TABLE 2   Thermal Conductivities of Pure
Molten Alkali Halides, Units are 10^{-4} cals/cm. sec.°C

Salt	T °C	κ
LiCl	670	10.88
	770	11.55
KCl	820	8.62
	870	9.85
LiBr	605	9.42
	701	9.42
NaBr	802	7.59
	850	7.78
KBr	788	6.99
	850	7.06
NaI	705	6.50
	800	6.63
KI	734	5.71
	835	6.28

predicted by the kinetic theory of collisional transport in fluids of molecules interacting via simple model potentials, such as the hard core or square-well potentials.[18,19] In addition the data indicates that the thermal conductivity increases with an increase in temperature although the increase varies considerably probably partly due to experimental inaccuracy. This unusual trend illustrates the importance of the unique ionic nature of molten salts. Filippov[3] has examined the thermal conductivity of 83 organic compounds of which only two, glycol and glycerol, had positive temperature dependence of thermal conductivity. Water also has a positive temperature dependence over a certain temperature range.

As yet there is no tractable molecular theory of transport for molten salts, so we cannot compare our results with theory. However, our results indicate that, unlike the surface tension, thermal expansivity and isothermal compressibility for which the scaled particle theory of hard spheres has been somewhat successful for the alkali halides,[20] the coulomb potential cannot be ignored in a theory of the thermal conductivity of molten salts.

The thermal conductivity values presented herein have been shown by Young and O'Connell[21] to obey, although with fairly

large deviations, a law of corresponding states that includes the alkali halides and alkali nitrates. They found that the same law of corresponding states correlates very well the experimental electrical conductivities, viscosities, densities and ionic diffusivities. It would be worthwhile to try to give a sound theoretical basis to their law. Due to the frequency of breakage of the quartz sheathing, only two or three readings were taken at each temperature. The accuracy of the method would probably be greater if the number of readings was substantially increased. The authors intend to examine more salts in the future and to obtain more data on those studied in this paper.

Acknowledgements

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