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PREDICTION OF THE THERMAL CONDUCTIVITIES OF FUSED SALTS

Summary

A method has been developed for the prediction of the thermal conductivities of fused salts and salt mixtures at their melting points. A further relation for the temperature dependence of the thermal conductivities of fused salts has also been developed, but final validation of this correlation awaits further high-temperature experimental data.

Nomenclature

A_{ϕ}	percent atomic contribution to the total thermal conductivity at the melting point = $100 (k_A/k_T)_M$
C_p	heat capacity of liquid at constant pressure
k	thermal conductivity, Btu/hr ft ² °F/ft
k_B	Boltzmann's constant, or gas constant per molecule
M	molecular weight, g/g-mol
$\bar{M}$	average molecular weight of a mixture, g/g-mol
m	mass of an electron
N	number of ions per molecule (from formula)
n	number of free electrons per unit volume
T	absolute temperature, °K = °C + 273.2°
x	mole fraction of a component in a mixture

τ	average time between electronic collisions
ρ	liquid density, g/cc
ν	mean vibration frequency of molecules
Σ	summation sign

Subscripts

A	atomic
e	electronic
I	ionic
i	ith component

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M at melting point
T total
1 at lower temperature T_1
2 at higher temperature T_2

Introduction

It is naturally desirable to have available prediction correlations for each of the thermal properties involved in design work. To date, no such generalized relation has been available for the thermal conductivities of fused salts and salt mixtures. This memorandum outlines the development of such a correlation.

It must first be recognized that the nature of molten salts is such that their total conductive heat transmission is composed of two distinct contributions -- the atomic or lattice portion, arising from the short-range atomic or molecular order present in liquids generally; and the ionic portion, arising from a drift of ions, and subsequent energy transfer, between the atoms. The lattice contribution in a fused salt mixture probably resembles that of an amorphous (glassy) material, where the thermal vibrations of each atom interact with those of the neighboring atoms and interchange energy by inelastic scattering. Long-range irregularity in the structure and its direct consequence, inelastic structure scattering, result in conductivities of amorphous materials which are low relative to those of well-ordered crystals.

The ionic contribution, on the other hand, is looked upon as an energy interchange resulting from the undirected motion of free charged ions--higher

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energy ions moving to colder (lower energy) regions and giving up their energy excess, while the reverse energy pickup occurs in the opposite direction. The case of fused salts is therefore intermediate between the cases of pure organic liquids, which are nonelectrolytes and whose conductivities are due solely to the atomic or lattice contribution; and of liquid metals, where the electron drift component (corresponding to the ion contribution for fused salts) is almost entirely dominant. Any correlation of molten salt thermal conductivities must therefore account for each of these contributions.

The large number of methods which was unsuccessfully tried will not be discussed here. Of all such attempts, only the following proved to be of value.

Discussion of Derivation and Results

An equation published in 1942 by Rao¹ was used to correlate the atomic portion only of the total conductivity. This relation, when converted to English engineering units, becomes:

$$(k_A)_M = 10.43 \frac{T_m^{1/2} \rho_M^{4/5}}{M^{9/5}} \quad (1)$$

This equation applies only to the newly formed liquid phase at its normal melting point, and a comparison of experimental and calculated conductivities for 13 nonelectrolytes -- 10 organics of all types and liquid sulfur, oxygen, and nitrogen -- gave an average error of 16.8%. Rao derived this relation by considering a liquid near its melting point as an assemblage of a large number of linear harmonic oscillators vibrating at some single mean frequency, and by assuming that communication of thermal energy takes

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place at each extreme vibration. The oscillating particles are pictured as vibrating about a slowly displaced equilibrium position with an amplitude which is comparable with the mean intermolecular separation. Rao used Lindemann's expression² for the mean frequency value ν . This relation involves a constant which was assumed to be, and generally is, the same for all types of molecules. It may be possible to slightly modify this constant for a particular class of substances, such as the fused salts, when more data become available.

Percent atomic contribution at the melting point, denoted by A_{ϕ} , was calculated from equation (1) for eight fused salts for which reasonably accurate experimental conductivity values³ are available -- mixtures No. 12, 14, 30, 35, 44, and 104, and HTS ("heat transfer salt") and NaOH. The T_m term of equation (1) was taken as the liquidus temperature for the mixtures, and M was obtained from.

$$\bar{M} = \sum_i x_i M_i \quad (2)$$

The results of this calculation follow:

Salt	$\bar{M}$	A_{ϕ}
No. 12	41.29	25.2
14	44.85	24.8
30	110.48	12.7
35	44.15	22.2
44	109.77	14.5
104	70.70	25.2
HTS	84.30	26.0
NaOH	40.0	99.7

The remainder of the total conductivity -- the ionic contribution -- was then correlated by means of a plot of A_{ϕ} vs $\bar{N}$, where:

$$\bar{N} = \sum_i x_i N_i \quad (3)$$

where $\bar{N}$ might be designated "average ion No." This plot is shown as Figure 1. The essentially linear portion between $\bar{N}$ of 2.0 and 3.5 may be represented by:

$$A_{\%} = 41.3 - 8.05\bar{N} \quad (4)$$

It is seen that with the exception of NaOH, all the points fits the indicated curve with good precision (average deviation = 2.5%). At an abscissa value of zero, indicating a nonelectrolyte, the percent atomic contribution is naturally 100, as there are no longer any ions present.

The extreme deviation of NaOH may be attributed to the intense hydrogen bonding of its hydroxyl (-OH) radicals. This bonding effectively reduces the ionic mobility to an extent such that essentially all of its conductivity is of the lattice nature.

Either percent atomic or percent ionic contribution may be used for the ordinate of Fig. 1, as they are relatable by:

$$k_T = k_A + k_I \quad (5)$$

The procedure, then, for estimating the total thermal conductivity of a fused salt at its melting point or of salt mixtures at their liquidus temperature is:

- (a) Calculate $(k_A)_M$ from eqn. (1).
- (b) Calculate $\bar{N}$ with eqn. (3).
- (c) Using Fig. 1 or eqn. (4), obtain $A_{\%}$.
- (d) Divide $(k_A)_M$ from step (a) by $\left(\frac{A_{\%}}{100}\right)$ from step (c) to obtain $(k_T)_M$.

Temperature Dependence

Very few data exist for the conductivities of the fused salts at higher temperatures. Comparisons of such experimental values with those calculated by a proposed temperature function are thus necessarily limited at this time. The function below gives indications of validity, but final verification must await more high temperature experimental data.

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Fig. 1. Thermal Conductivity of Fused Salts at T_M

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The Wiedemann-Franz-Lorenz equation, relating thermal and electrical conductivities and their variation with temperature for some crystalline metals, was tried in many forms, but as expected, failed.

A. H. Wilson⁴ has correlated the electronic contribution to the thermal conductivity of liquid metals by:

$$k_e = \frac{\pi^2}{3} \cdot \frac{n k_B^2 T}{m} \quad (6)$$

Assuming correspondence of the electronic contribution in liquid metals and of the ionic contribution in molten salts, and by applying classical kinetic theory to the ion behavior, the following may be obtained from eqn. (6):

$$k_I \propto \rho \sqrt{T} \quad (7)$$

which gives the temperature dependence of the ionic portion of the total conductivity for fused salts.

The temperature dependence of the atomic contribution may be obtained from any one of several fairly accurate relations for organic liquids, whose conductivities are 100% atomic. A relation derived from the work of Sakiadis and Coates⁵ was chosen as possibly the most satisfactory:

$$k_A \propto c_P \rho^{5/3} \quad (8)$$

Combination of equs. (7) and (8) gives the final postulated temperature function:

$$\left(\frac{k_{T2}}{k_{T1}} \right) = (F.A.)_1 \left(\frac{\rho_2}{\rho_1} \right)^{5/3} \left(\frac{c_{P2}}{c_{P1}} \right) + (F.I.)_1 \left(\frac{\rho_2}{\rho_1} \right) \left(\frac{T_2}{T_1} \right)^{1/2} \quad (9)$$

where F.A. denotes "fraction atomic" and

F.I. "fraction ionic".

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The following values were calculated³ from eqn. (9) for three fused salt mixtures -- Nos. 12, 30, and 44 -- for a temperature of 900°C (1652°F):

<u>Salt Mixture</u>	<u>k_M</u>	<u>k 900°C, calc.</u>	<u>% Change</u>
12	2.6	2.58	-0.7
30	1.3	1.36	+4.7
44	1.2	1.28	+6.4

It is seen that if the derived relation is valid, the thermal conductivities of the fused salts of interest are relatively temperature-independent, increasing only slightly with temperature.

Further Work

An attempt will be made to check the generality of the correlation of conductivities at the melting point as new data become available. In particular, the conductivity results of the recently begun chloride mixture program will be checked against this relation. Further, a mixture with a high value of $\bar{N}$ (>3.5) will be synthesized and its conductivity determined in an effort to extend the range of variables of Fig. 1. Naturally, an $\bar{N} < 2$ cannot practicably be obtained. Higher temperature conductivity results will be checked against the proposed temperature function -- eqn. (9).

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