in counter-phase to m_0 should increase somewhat with m_0, or the ionic radius, for Li^+, Na^+ and Ag^+.

D_0 for K^+, Tl^+ and Rb^+ is much lover than for the other impurity cations, which means that the masses m' and m'' are much larger than for self-diffusion and this supports the idea that these ions mainly are mobile in defects in the sulphate lattice[5]. The somewhat lower Q values for Na^+ and Ag^+ than for self-diffusion can then be explained by assuming some defect diffusion also for these ions.

Lundén and Olsson[9] have recently reported some thermal diffusion coefficients. For Na^+ and Ag^+, and also for Li^+, the Soret coefficient is small in f. c. c. Li_2SO_4, compared with K^+ and Rb^+. This supports our model with two diffusion mechanisms, where defect diffusion gives a much higher Soret coefficient than lattice diffusion.

This work was financially supported by the Swedish Technical Research Council.

Optical Determination of Thermal Conductivity with a Plane Source Technique

II. Molten $LiNO_3$, $RbNO_3$, and $CsNO_3$

Silas E. Gustafsson, Nils-Olov Halling, and Rolf A. E. Kjellander

Department of Physics, Chalmers Institute of Technology, Göteborg, Sweden

(Z. Naturforsch. **23 a**, 682—686 [1968]; received 20 December 1967)

The thermal conductivity and the thermal diffusivity of the three alkali nitrates $LiNO_3$, $RbNO_3$ and $CsNO_3$ have been measured over a temperature range between 50° and 100 °C above their melting points. Any temperature dependence of the thermal conductivity cannot be established for any of the investigated liquids but the results indicate that it must be less than 10^{-3} °C^{-1}. The experimental results are compared with the conductivities which can be calculated with already excisting theories. A somewhat modified theoretical approach is suggested for estimating the thermal conductivity, where no adjustable parameters are being used. The experimental and theoretical values at the melting points agree within about 10 percent.

The plane source technique combined with a suitable optical method has proved to be very useful when determining the thermal conductivity and the thermal diffusivity of transparent liquids and particularly molten salts[1–3]. Experimental investigations of these thermal properties of ionic liquids are very rare, and this is obviously due to the tedious nature of the measurements and the large errors which can be encountered[4, 5].

In an earlier paper[2] we have described the experimental technique in detail, and the same procedure has been used in this investigation. The only difference was that in order to limit the amount of salt we had to redesign the container of the liquid, and furthermore it appeared to be much more convenient to work with a foil which was horizontally suspended. To keep the foil stretched we used two glass cylinders connected to a square of stainless steel metal which was placed on top of the foil and at the same time worked as a lid of the cell. This reorientation of the foil cannot be made without changing the convection stability of the liquid. It is thus likely that the convection starts earlier than when the foil is vertically oriented if comparing with the situation in a hot wire cell. Bryngdahl[6] has reported that the onset of convection in water appeared in his cell after 6 seconds with a vertical wire and after about 3 seconds with a horizontal one, if the output of power per unit length of the wire was about 50 J/s·m. It would be rather useless to try to change the characteristic dimension in the expression which gives the maximum time of an experiment as derived earlier[1], because the effect of changing the orientation of the foil can simply be described by a different value of the Rayleigh number R. To estimate this quantity we made a number

---

[1] S. E. Gustafsson, Z. Naturforsch. **22 a**, 1005 [1967].

[2] S. E. Gustafsson, N.-O. Halling, and R. A. E. Kjellander, Z. Naturforsch. **23 a**, 44 [1968].

[3] S. E. Gustafsson and R. A. E. Kjellander, Z. Naturforsch. **23 a**, 242 [1968].

[4] H. Bloom, A. Doroszkowski, and S. B. Tricklebank, Austral. J. Chem. **18**, 1171 [1965].

[5] A. G. Turnbull, Austral. J. Appl. Sci. **12**, 30, 324 [1961].

[6] O. Bryngdahl, Arkiv Fysik **21**, 289 [1962].

of experiments at room temperature with water which from point of view of convection has somewhat similar properties as molten nitrates. It turned out that one should use a value in the neighbourhood of $R = 400$ for this particular geometry independent of the liberation of heat per unit length of the plane source. This has the consequence that the time of a particular run is reduced to about 2/3 of the available time in earlier experiments. During the investigation of molten salts it turned out that we could measure over at least ten seconds in all the liquids being studied. This time is of course very dependent on the properties of the liquid. $LiNO_3$, for instance, has close to the melting point a very high viscosity which gives a rather long time before the convection starts.

The orientation of the foil is thus not very important from experimental point of view and the reduction of the time before the onset of convection does not measurably influence the accuracy of the determination.

Experimental

The experimental setup and the procedure are described in an earlier paper[2]. The foils were made of silver and platinum with the approximate dimensions $0.010 \times 40 \times 80$ mm^3. A silver foil was used when investigating $RbNO_3$ but in $LiNO_3$ and $CsNO_3$ we could only use a platinum foil because of the corrosion of the silver metal in the melt.

$LiNO_3$ was of analytical reagent quality while $RbNO_3$ and $CsNO_3$ were of C. p. grade.

When determining the thermal conductivity it is necessary to measure the output power per unit length of the foil with a high accuracy. The total output power can be measured very accurately with a fast *xy*-recorder but it is rather difficult to get the length of the foil since it is spotwelded to heavier pieces of the same metal. In order to improve this measurement we determined the weight of the foil which had a well defined length before fixing it in its position. When the foil was welded to the metal pieces the electrical resistance of the foil was measured. By using these data it was possible to compute the length of the foil from known values of the density and the resistivity of the material. The lengths we obtained in this way agreed very well with the direct measurements.

Experimental Results

We have measured the thermal diffusivity and the thermal conductivity of molten $LiNO_3$, $RbNO_3$ and $CsNO_3$. In order to get as reliable results as possible a couple of determinations at approximately the same temperature were made as can be seen from Table 1. Some of the points are mean values of a number of measurements.

Temp. °C	Output of power per unit length of the foil J/m·sec	Thermal diffusivity mm^2/sec	Thermal conductivity J/m·sec °C
	$LiNO_3$		
259.5	44.86	0.171	0.636
259.5	45.11	0.169	0.651
279.5	46.26	0.154	0.626
279.7	46.13	0.169	0.630
307.9	47.40	0.152	0.650
308.1	47.53	0.174	0.633
308.1	47.66	0.151	0.637
	$RbNO_3$		
323.1	25.90	0.120	0.353
323.3	25.95	0.123	0.359
323.5	25.95	0.125	0.356
347.7	26.70	0.118	0.361
347.8	26.77	0.114	0.356
347.8	26.78	0.123	0.365
361.8	27.31	0.119	0.363
361.9	27.11	0.118	0.357
362.0	27.13	0.125	0.354
382.8	27.91	0.121	0.357
382.9	27.90	0.117	0.357
382.9	28.17	0.124	0.363
402.7	28.69	0.131	0.344
402.8	28.95	0.132	0.343
	$CsNO_3$		
413.7	20.92	0.120	0.330
413.9	21.00	0.117	0.343
418.9	21.12	0.114	0.337
419.0	21.12	0.115	0.331
419.1	21.22	0.111	0.331
424.8	21.36	0.118	0.336
424.9	21.25	0.110	0.333
425.1	21.18	0.131	0.346
443.0	21.64	0.121	0.339
443.1	21.72	0.128	0.346
443.1	21.73	0.120	0.342
457.2	22.00	0.134	0.347
457.7	21.99	0.106	0.328
457.7	22.09	0.115	0.336
476.3	22.58	0.123	0.331

Table 1. Thermal conductivity and thermal diffusivity of alkali nitrates above the melting point.

We have assumed a linear relationship between the thermal properties and the temperature. In Table 2 the temperature dependence of the diffusivity and the conductivity is given, where we have taken the melting point as a reference temperature. Our temperature dependences appear to be much smaller than the ones indicated by the experimental

Salt	Thermal diffusivity mm²/sec	Thermal conductivity J/m·sec·°C
$LiNO_3$	$0.1695-21\ \cdot 10^{-5}\,(t-254)$	$0.6379-0.1\cdot 10^{-4}\,(t-254)$
$NaNO_3$	$0.1642+\ 1.1\cdot 10^{-5}\,(t-310)$	$0.5125+4.4\cdot 10^{-4}\,(t-310)$
KNO_3	$0.1770-\ 0.8\cdot 10^{-5}\,(t-337)$	$0.4815+0.9\cdot 10^{-4}\,(t-337)$
$RbNO_3$	$0.1186+\ 0.1\cdot 10^{-5}\,(t-316)$	$0.3610-1.1\cdot 10^{-4}\,(t-316)$
$CsNO_3$	$0.1169+\ 9.0\cdot 10^{-5}\,(t-414)$	$0.3369+1.0\cdot 10^{-4}\,(t-414)$

Table 2. Temperature dependence of thermal diffusivity and thermal conductivity expressed by means of an equation of the form $y=a+b(t-t_m)$, where a and b are constants and t_m is the melting point in °C.

values from two earlier reports[4, 5]. A possible explanation of a large positive temperature dependence may be increasing danger of convection at higher temperatures which cannot be directly checked in an experiment with for instance the "hot wire cell" unless an optical technique is used. Especially we do not find any pronounced deviation from linearity of the thermal conductivity as a function of temperature above the melting point, which is reported by TURNBULL[5]. When investigating $CsNO_3$ we worked particularly close to the melting point in order to discover this effect, but no significant deviation was observed.

Theory and Discussion

Thermal conductivity data may cast some light on the basic molecular processes involved in this and similar transport phenomena. Because of the complexity of the process[7] we are forced to work with very simple models and examine a number of theories which will be used for calculating the thermal conductivity of the alkali nitrates. Even if these approaches are not very sophisticated they may still be capable of bringing out some details of the mechanism involved and may therefore be of importance when establishing the foundations of a more rigorous theory in the future.

BRIDGMAN[8] is using a very simple physical picture, where he images the particles (atoms and ions) in a cubical arrangement and the energy difference between two adjacent particles (in the direction of the temperature gradient) being handed down the row of particles with the speed of sound, u, leading to a thermal conductivity of

$$\Lambda = 3\,k\,u\,l^{-2} \qquad (1)$$

where k is the Boltzmann constant, and l is the interparticle distance. For ionic melts it is appropriate to take l as $(V/N\,n)^{1/3}$, where V is the molar volume, N Avogadro's number and n the number of discrete ions of the dissociated molten salt.

A straight forward application of the kinetic theory of gases is used by KINCAID and EYRING[9] to get an estimation of the thermal conductivity. The formula has the same form as the one used by BRIDGMAN apart from a coefficient, which originates from the correction factor derived by LOEB for the thermal conductivity of gases. This leads to the expression

$$\Lambda = 0.931\,(1/\gamma)^{1/2}\cdot 3\,k\,(N\,n/V)^{2/3}\cdot u \qquad (2)$$

where γ is the ratio between the specific heat at constant pressure and the specific heat at constant volume. The agreement between the calculated and experimental values is surprisingly good for a number of liquids at room temperature.

A different approach is suggested by RAO[10] and HORROCKS and McLAUGHLIN[11] who imagine the energy transport in two disctinct ways, (a) by a vibrational mechanism and (b) by a convective mechanism. The vibrational contribution to the thermal conductivity is due to the energy being transferred when two vibrating particles "collide" in the quasilattice. This is supposed to occur with the mean vibrational frequency ν. The convective contribution originates from the hopping of particles from "occupied sites" to "vacancies" in the liquid. This last contribution is proportional to the self diffusion coefficient D and can be shown to be negligible in most liquids (Table 3). The final expression becomes

$$\Lambda = \Lambda_{\text{vib}} + \Lambda_{\text{conv}} = 2\,\nu\,c_v\,l^{-1} + 2\,D\,c_v\,l^{-3} \approx 2\,\nu\,c_v\,l^{-1}. \qquad (3)$$

c_v is the specific heat at constant volume, in the following taken as $3\,k$, assuming six vibrational degrees of freedom.

---

[7] S. A. RICE, Trans. Faraday Soc. **58**, 499 [1962].

[8] P. W. BRIDGMAN, The Physics of High Pressures, G. Bell & Sons, London 1949.

[9] J. F. KINCAID and H. EYRING, J. Chem. Phys. **6**, 620 [1938].

[10] M. R. RAO, Phys. Rev. **59**, 212 [1941].

[11] J. K. HORROCKS and E. McLAUGHLIN, Trans. Faraday Soc. **56**, 206 [1960].

Salt	Calculated values (J/sm °C)							Experimental values J/sm °C	Convective contribution Eq. (3) %
	BRIDGMAN Eq. (1)	KINCAID, EYRING Eq. (2)	TURNBULL Eq. (6)	Harmonic oscillator Eq. (8) $r_N = 1.64$ Å	Rectangular cell potential model. Eq. (9)				
					Free volume [14]	$r_N = 1.64$ Å	Different r_N-values		
$LiNO_3$	0.759	0.665	0.647	0.609	0.837	0.541	0.655	0.638	0.81
$NaNO_3$	0.675	0.590	0.557	0.533	0.687	0.484	0.498	0.512	0.84
KNO_3	0.573	0.489	0.460	0.572	0.638	0.499	0.459	0.482	0.55
$RbNO_3$	—	—	0.351	0.471	—	0.407	0.373	0.361	—
$CsNO_3$	—	—	0.298	0.442	—	0.380	0.348	0.337	0.50

Table 3. Thermal conductivity of the alkali nitrates at the melting point.

To be able to use Eq. (3) we now have to estimate the mean vibrational frequency ν. By using various interparticle potentials it is possible to get a number of approximations of the frequency. We will here discuss a few approaches which are fairly easily applied to ionic liquids and which do not require parameters unknown for these melts.

A model based on the assumption that the ions behave as harmonic oscillators is developed by LINDEMANN [12]. The determination of the frequency is accomplished by the introduction of the Einstein expression of the specific heat and gives

$$\nu = (\pi\, s\, l)^{-1}\,(2\,k\,T_{\mathrm{m}}/m)^{\frac{1}{2}}\,[1 - h(\pi\, s\, l)^{-1}\,(8\,m\,k\,T_{\mathrm{m}})^{-\frac{1}{2}}] \approx (\pi\, s\, l)^{-1}\,(2\,k\,T_{\mathrm{m}}/m)^{\frac{1}{2}}\,. \qquad (4)$$

T_{m} is the melting point, m is the weight of the ion, $s\,l$ equals the interionic distance minus the sum of the radii of the anion and the cation, and h is Planck's constant. In view of the approximate nature of all such estimations the second term within the main brackets of Eq. (4) is neglected by LINDEMANN and this seems even more justified in our case were the melting point is much higher. A rough estimation shows that the maximum contribution from this term is of the order of 4 percent. Combining Eq. (3) and Eq. (4) we get a final expression of the thermal conductivity

$$\Lambda = 6\,k\,(\pi\, s\, l^2)^{-1}\,(2\,k\,T_{\mathrm{m}}/m)^{\frac{1}{2}}\,. \qquad (5)$$

The estimation of the s parameters is rather critical when using this formula. LINDEMANN himself assumes that s is constant for all substances and RAO [10] and TURNBULL [5] do the same thing. In the application of what would correspond to Eq. (5) to molten salts TURNBULL only considers the variation of T_{m}, $m = M/n$, where M is the molecular weight, and $l^2 = (V/N\,n)^{2/3}$. The rest is lumped together in a constant, which is estimated from available values of Debye frequencies of a number of alkali halides. His final expression turns out to be

$$\Lambda = 1.19 \cdot [T_{\mathrm{m}}/(M/n) \cdot (V/n)^{4/3}]^{\frac{1}{2}}. \qquad (6)$$

Still another approach is to use one of the simplest models of the liquid state, the rectangular cell potential model [13], which can be used to calculate the frequency. This model of a rigid particle in a box with a specific heat of $3\,k/2$ gives with our symbols

$$\nu = (4\,s\,l)^{-1} \cdot (8\,k\,T/\pi\,m)^{\frac{1}{2}}\,. \qquad (7)$$

This equation combined with Eq. (3) gives an expression of the thermal conductivity very similar to Eq. (5). The only difference is actually a numerical constant.

The Eqs. (4) and (7) contain the mass m of a particular ion in the melt. This is, however, not a well defined quantity when cation and anion have different masses. Hence, for a liquid electrolyte we have to use an effective value of $m = (M_{\mathrm{c}} \cdot M_{\mathrm{a}}/N^2)^{\frac{1}{2}}$, where M_{c} and M_{a} are the ionic weights of the cation and anion [14]. It should be mentioned here that TURNBULL is using a mean value of the ionic weights which can be seen from his formula Eq. (6). Introducing the proper m-values in Eq. (4) and Eq. (7) we finally get the expressions to be used

$$\Lambda = 6\,k\,(\pi\, s\, l)^{-1}\,(n\,N/V)^{1/3}\,[2\,k\,T_{\mathrm{m}}\,N/(M_{\mathrm{c}} \cdot M_{\mathrm{a}})^{\frac{1}{2}}]^{\frac{1}{2}}, \qquad (8)$$

$$\Lambda = 6\,k\,(2\,\pi^{\frac{1}{2}}\, s\, l)^{-1}\,(n\,N/V)^{1/3}\,[2\,k\,T\,N/(M_{\mathrm{c}} \cdot M_{\mathrm{a}})^{\frac{1}{2}}]^{\frac{1}{2}}. \qquad (9)$$

---

[12] F. A. LINDEMANN, Phys. Z. **11**, 609 [1910].

[13] J. K. HORROCKS and E. MCLAUGHLIN, Trans. Faraday Soc. **59**, 1709 [1963].

[14] J. O'M. BOCKRIS and N. E. RICHARDS, Proc. Roy. Soc. London **241**, 44 [1957].

These equations contain the s-parameter which LINDEMANN assumed to be constant. His assumption cannot be physically justified even if we limit ourselves to one particular class of liquids. On the other hand this quantity is rather difficult to estimate. One way to get a fairly good approximation is to use the free volume estimations of the liquid, which must be related to s in a rahter simple manner. The problem in our case is that there are very few experimental determinations of this quantity for molten alkali nitrates. There is of course a possibility to estimate s from the interionic distance l and the radii of the cation and the anion. This estimation should not be too difficult to make for such ionic melts as the molten alkali halides but in this particular case we must know the radius of the nitrate ion, which may be expected to behave differently depending upon the radius of the cation which is present. When considering the geometry of a nitrate ion being coplanar, it does not seem too unrealistic to assume a varying "effective" ionic radius r_N. However, when computing the thermal conductivity from Eqs. (8) and (9) we have assumed a constant value of 1.64 Å. The calculated values are shown in Table 3 and the agreement is fairly good even if the theory in this case cannot explain the large variation of the thermal conductivity among the alkali nitrates, which may be due to the incompletion of the theory and the approximations used in its development. There is, however, another circumstance which supports the assumption of varying r_N and that is the variation of r_N when it is calculated from the free volumes reported by BOCKRIS and RICHARDS[14]. The values obtained from their free volumes are given in Table 4 together with a series of adjusted values, which have been calculated from our thermal conductivity data using Eq. (9) and the tabulated values of the radii of the cations. It is of course impossible to say that this is a significant departure from a constant radius of the nitrate ion in view of the approximate nature of the whole development, but the difference between two successive adjusted values is not very different from the one given by the free volume estimation. The observation of a varying "effective" radius in a nitrate melt by DE NOOIJER[15] should also be mentioned here. In view of this tendency we started with a mean value (1.64 Å) of the radii of the anions but assumed a distribution of the separate r_N-values according to the free volume variation. The results are shown in column 8 of Table 3 and the agreement happens to be much better than one would expect from this simple theory. As to the agreement between the TURNBULL equation and the experimental results we must remember that he is using a different expression of the mass of an ion, which makes a rather big difference specially for $LiNO_3$. It is interesting to note the good agreement between the calculated values from the Kincaid-Eyring formula and the measured data, which shows that BRIDGMAN's original approach was substantially in order and that it may be meaningful to estimate the speed of sound from thermal conductivity data.

Salt	Radii of cations Å	Radii of anions Ref. [14] Å	Radii of anions Adjusted values Å
$LiNO_3$	0.68	1.97	1.77
$NaNO_3$	0.97	1.84	1.68
KNO_3	1.33	1.77	1.62
$RbNO_3$	1.47	—	1.57
$CsNO_3$	1.67	—	1.57

Table 4. Radii of the ionic species of the melts.

In conclusion we would like to once more stress the difficulty of using this simple theory as expressed by Eqs. (8) and (9) because of the critical estimation of the distance $s\,l$. However, it must be more satisfactory to try to estimate this quantity than to introduce an adjustable parameter which has no physical meaning whatsoever. Work is now in progress to extend the temperature range of these measurements so that it will be possible to investigate the thermal properties of molten alkali halides. These melts have a much simpler structure, which makes it more meaningful to try a comparison between experimental and calculated values of the thermal conductivity.

Acknowledgement

This investigation is supported by the Swedish Council for Applied Research.

---

[15] B. DE NOOIJER, The Electrical Conductivity of Molten Nitrates and Binary Nitrates, Thesis, Amsterdam 1965.