

## Optical Determination of Thermal Conductivity with a Plane Source Technique

I. Molten Sodium Nitrate and Potassium Nitrate

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A recently developed plane source method for non-steady-state measurements of the thermal conductivity and thermal diffusivity of transparent liquids is now being applied to the study of molten salts. In these first measurements sodium nitrate and potassium nitrate have been investigated from their melting points to about 450°C. No temperature dependence of the thermal diffusivity can be established for either of the liquids, whereas the thermal conductivity in both cases increases very slowly with the temperature.

A description of the experimental arrangement is included.

A newly developed non-steady-state method<sup>1</sup> consisting of a wave-front-shearing interferometer used to record the temperature distribution close to a plane heat source is believed to be particularly useful in the study of the thermal diffusivity and thermal conductivity of ionic melts, firstly, because the voltage drop across the "hot foil" can be kept as low as 20 mV/cm which means that it is possible to work well below the decomposition voltage and thus avoid current flow and heating in the salt<sup>2</sup>, and secondly, because the temperature control of the thermostat is less important and a small drift of the temperature may be acceptable as long as the gradient is negligible compared with the one established in the liquid by the heat source.

As to the use of optical interferometry to study certain transport properties of molten salts, it is interesting to note that there exists a large number of different methods to measure diffusion, thermal diffusion and thermal conductivity but nobody ever used interferometric techniques although they have proved very useful in precise work at room temperature. They are of course limited to transparent liquids which preferably have large changes of the refractive index with temperature and composition. These requirements are, however, very well fulfilled for most of the molten salts<sup>3</sup>. The possible temperature range of the measurements is of course limited by optical disturbances due to the thermal radiation

from the melt itself, but it may be possible to reach a temperature of about 1000°C<sup>4</sup>. The main reason why optical interferometry has not been used in high temperature work is the difficulty to construct a thermostat and a container for the liquid to be studied. The design of the furnace must be such that it allows the light to pass without distortion of the wave-front and this is rather difficult because of the great temperature gradients in the walls of the furnace. In this work we have used "light channels" through the walls of the thermostat each consisting of a stainless steel tube with two quartz plates at the ends (Fig. 1). By lowering the air pressure to a few tenths of a mm Hg inside the channels no disturbance whatsoever could be detected with the interferometer. The cell (Fig. 2) containing the molten salt was made of stainless steel with carefully ground end surfaces covered with optically flat quartz windows on the outside.

### Experimental

The chemicals were of analytical reagent quality (E. Merck) giving clear, colorless melts. The handling of the salts and the temperature measurements are discussed elsewhere<sup>3</sup>.

In Fig. 1 a detailed description of the cylindrical thermostat is given. The construction is rather conventional with electrical heating from a stabilized AC voltage source and water cooling on the outside. The essential modification is

<sup>1</sup> S. E. GUSTAFSSON, Z. Naturforsch. **22 a**, 1005 [1967].

<sup>2</sup> A. G. TURNBULL, Austr. J. Appl. Sci. **12**, 30, 324 [1961].

<sup>3</sup> L. W. WENDELÖV, S. E. GUSTAFSSON, N.-O. HALLING, and R. A. E. KJELLANDER, Z. Naturforsch. **22 a**, 1363 [1967].

<sup>4</sup> J. ZARZYCKI and F. NAUDIN, C. R. Acad. Sc. Paris **256**, 1282 [1963].



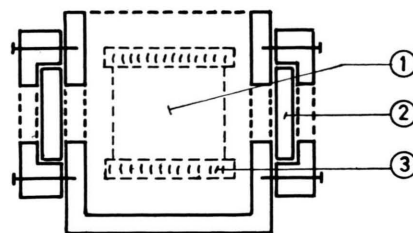
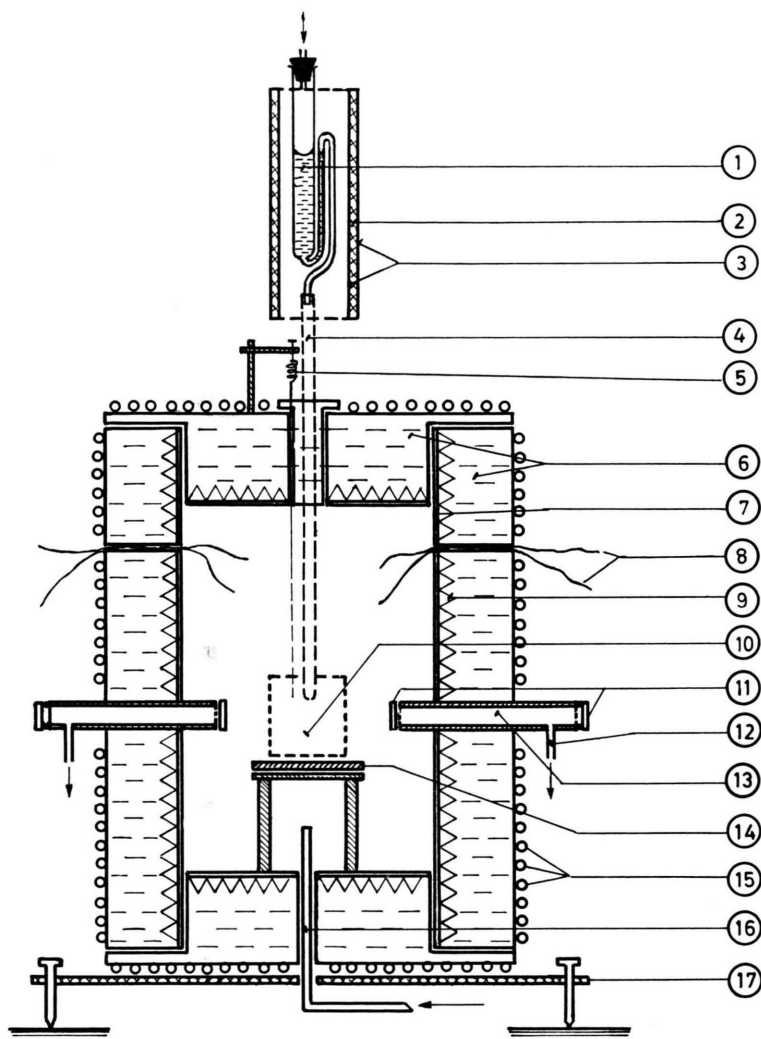


Fig. 2. Container for the fused salt. 1. Metal foil. 2. Quartz window. 3. Quartz cylinder.

the introduction of the "light channels" in the walls. Above the furnace the arrangement for introducing the molten salt into the cell is shown. It turned out to be necessary to fuse the salt before putting it into the cell in order to get perfectly clear melts.

The optical system is the same as we used in earlier measurements<sup>1</sup>. The magnification can be determined by introducing a silver plate of known width into the liquid close to the metal foil.

When measuring the thermal conductivity it is necessary to know the heat liberation per unit length of the foil and this was obtained with a fast xy-recorder (Moseley 2D-2AM) giving the voltages across the foil, which was spotwelded to heavy silver joints, and a standard resistor in the main circuit. The foil was passed across two cylindrical glass tubes (Fig. 2) and in order to keep it plane during operation we had to apply a small stress from a spring outside the furnace (Fig. 1). The approximate dimensions of the foils

were:  $0.009 \times 32 \times 86 \text{ mm}^3$  silver foil when working with  $\text{KNO}_3$  and  $0.010 \times 40 \times 86 \text{ mm}^3$  platinum foil when working with  $\text{NaNO}_3$ .

### Deviations from Theory

In the mathematical treatment of the heat conductivity around a plane heat source and in the derivation of the optical path a number of simplifying assumptions had to be made<sup>1</sup>. We assumed for instance that the heat source did not have any thickness (plane source) and that both the thermal diffusivity and the output of power per unit area of the plane source were constant during an experiment. This means that we did not take into consideration such effects as the power necessary to

raise the temperature of the foil itself, the temperature dependence of the thermal diffusivity, and the thermal radiation from the foil. Since we now are investigating a different class of liquids at a much higher temperature, it is necessary to consider these effects in some detail. We refer here to the equations and symbols used in an earlier paper<sup>1</sup>.

The influence of the thickness of the foil, as expressed by the ratio of  $Q_t/Q$ , becomes a little higher when working with these molten salts because the density times the specific heat ( $\rho \cdot c_p$ ) is smaller than that of water by a factor 0.7. In these experiments we have been working with foils of a thickness not exceeding 0.01 mm which means that  $Q_t/Q$  has decreased to the order of  $6 \times 10^{-3}$  after 1 second. It is thus safe to use the interferograms, which are recorded after about 2 seconds, to determine the thermal conductivity.

Another thing which may cause the liberation of heat not to be constant is the thermal radiation from the foil which may be estimated from the ratio  $Q_r/Q$ . This is also increased by the decrease of  $\rho \cdot c_p$  but the largest contribution comes from the fact that the absolute temperature is higher by a factor 2.5.  $Q_r/Q$  increases as the square root of the time ( $t$ ) which means that it is preferable to measure over a short period of time. Taking a  $t$ -value of 10 seconds  $Q_r/Q$  is then of the order of  $3 \times 10^{-3}$  where we have assumed  $\varepsilon \approx \alpha_{12} \approx 0.02$  which is a constant being very difficult to estimate. It should be mentioned here that in the derivation of Eq. (10) in reference <sup>1</sup> the mean value should of course be taken over  $-d \leq y \leq d$  giving the same final result.

The temperature increase in the liquid may be estimated by computing  $\Delta T_x$  from the expression containing the output of power per unit length of the foil. This average of the temperature increase is computed for a cellwidth of  $l = d + 10$  mm giving for all the measurements on both  $\text{NaNO}_3$  and  $\text{KNO}_3$  approximately  $\Delta T_x = 0.06$  °C which is such a low value that it has not been taken into account when giving the absolute values of the temperatures in the tables.

The effect that ultimately limits the time of an experiment is the onset of convection in the liquid. It is possible to estimate this time by using the expression of  $t_c$  and choosing a value of the Rayleigh number ( $R$ ) in the neighborhood of 1000. If we use the value  $R = 930$  obtained in our earlier work,  $t_c$  becomes  $(13 \pm 1)$  sec for  $\text{KNO}_3$  and  $(17 \pm 1)$  sec for

$\text{NaNO}_3$ . The error expresses the fact that  $t_c$  is a function of temperature, due to the temperature dependence of the viscosity and the thermal expansion. This seems to be in rather good agreement with the experimental observations for these molten salts. When evaluating the measurements we never used the interferograms recorded later than 10 seconds from the start of an experiment. In this region the plots of  $x^2$  versus  $t$  were perfectly straight lines indicating no sign of convection.

## Results and Discussion

Table 1 shows the thermal diffusivity and thermal conductivity of molten sodium nitrate. No temperature dependence of the thermal diffusivity can be established from these measurements. In his excellent review<sup>5</sup> McLAUGHLIN has given a set of recommended values for the thermal conductivity of molten  $\text{NaNO}_3$  which are quoted in column six where we have assumed a linear temperature dependence. It is easily seen that the deviation of our values from the recommended ones (column seven), which is on the average 2.8%, is mainly due to a slightly higher temperature dependence.

In Table 2 the results of the measurements on  $\text{KNO}_3$  are presented. For this liquid there are no best values due to the large discrepancies between the data of the few experimenters. In this case we have made a number of experiments (2–4) at the same temperature in order to be able to estimate the reproducibility of the measurements. The mean deviation is given for both the thermal diffusivity ( $\kappa$ ) and the thermal conductivity ( $\lambda$ ) indicating that it is easier to get  $\lambda$  with high accuracy than  $\kappa$ . However, in order to compute  $\lambda$  it is necessary to know  $\kappa$  if we do not want to resort to published values of the density and the specific heat. The reason why we get better accuracy in the determination of  $\lambda$  is the relative insensitivity of  $\lambda$  to an error of  $\kappa$ , which is easily shown by a straight forward error calculation. As a matter of fact, an error in  $\kappa$  of say 3% means only an error of 1.5% in  $\lambda$ , which is nicely demonstrated in the table where the mean deviation of  $\kappa$  is on an average 2.7% while the corresponding value of  $\lambda$  is 1.3%. These last figures also show that the error in the determination of the power supplied to the foil is negligible.

<sup>5</sup> E. McLAUGHLIN, Chem. Rev. **64**, 389 [1964].

Temp. °C	Power output per unit length of the foil J/m sec	Thermal diffusivity mm <sup>2</sup> /sec	Thermal conductivity J/m sec °C	Specific heat cal/gm °C	Recommended values of thermal conductivity J/m sec °C	Deviation from recommended values %
315.1	41.35	0.162	0.511	0.360	0.543	— 5.9
325.4	41.34	0.163	0.498	0.350	0.544	— 8.5
336.3	42.78	0.161	0.527	0.376	0.545	— 3.3
347.3	43.45	0.164	0.548	0.385	0.545	0.6
366.9	44.26	0.171	0.548	0.372	0.547	0.2
377.2	44.66	0.171	0.546	0.372	0.548	— 0.4
399.4	45.32	0.166	0.544	0.385	0.549	— 0.9
423.8	47.13	0.163	0.561	0.407	0.551	1.8
453.4	48.19	0.163	0.571	0.419	0.553	3.3

Table 1. Thermal conductivity and thermal diffusivity of molten sodium nitrate.

Temp. °C	Power output per unit length of the foil J/m sec	Thermal diffusivity mm <sup>2</sup> /sec	Mean deviation %	Thermal conductivity J/m sec °C	Mean deviation %	Specific heat cal/gm °C
338.0	36.57	0.177	4.2	0.470	1.5	0.339
344.5	36.96	0.176	6.4	0.487	1.4	0.354
365.6	38.18	0.176	3.6	0.492	1.6	0.361
388.8	39.13	0.177	0.5	0.487	0.9	0.358
406.7	39.85	0.177	3.7	0.487	1.1	0.361
422.8	40.61	0.180	1.6	0.497	1.0	0.365
445.3	41.56	0.175	1.4	0.477	1.9	0.363
451.0	43.46	0.174	0.5	0.498	0.9	0.382

Table 2. Thermal conductivity and thermal diffusivity of molten potassium nitrate.

This discussion shows that the determination of the thermal conductivity and the thermal diffusivity may be considered relatively independent, which gives us a possibility to estimate the specific heat ( $c_p$ ) from the relation  $\lambda = \rho \cdot c_p \cdot \kappa$ . The  $c_p$ -values given in the tables indicate a slight temperature dependence and an extrapolation to the melting point gives a value which is not too far off the calorimetrically obtained one. This may be taken as an indication of the internal consistency of our measurements. Here it may be appropriate to consider all the errors in the determination of the two transport coefficients. In the measurements of  $\kappa$  we do not have just the error indicated in Table 2, but also the uncertainty in the determination of the magnification which is estimated to 0.3%. When measuring  $\lambda$  we must consider errors in the length of the foil 0.7%, in the shearing 0.5%, and in the temperature dependence of the refractive index

0.1% giving an estimated error in  $\kappa$  of 3.0% and in  $\lambda$  of 2.6%. This means that we should expect an error of the order of 6% in the specific heat.

It may also be mentioned here that our thermal conductivity values of  $\text{KNO}_3$  are distributed between those of BLOOM, DOROSZKOWSKI, and TRICKLEBANK<sup>6</sup> and those of TURNBULL<sup>2</sup> with a temperature dependence which is of the same order of magnitude as for  $\text{NaNO}_3$  ( $8 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$  for  $\text{NaNO}_3$  and  $2 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$  for  $\text{KNO}_3$ ).

This investigation has shown the applicability of interferometric techniques to the study of certain transport properties at elevated temperatures. We believe this to be a contribution to the development of reliable techniques to be used in precise work when investigating this particular class of liquids.

#### Acknowledgement

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<sup>6</sup> H. BLOOM, A. DOROSZKOWSKI, and S. B. TRICKLEBANK, *Austr. J. Chem.* **18**, 1171 [1965].