whereas the present extrapolation gives 12,337 cal mol^{-1}. The difference, 41 cal, represents an uncertainty or, if the present work be accepted, an error in the heat of fusion. It is not large, but since Clark estimated the uncertainty as 20 cal, it is worth noticing.

Literature Cited

(1) Bartholomew, R. F., *J. Phys. Chem.*, **70**, 3442 (1966).
(2) Bizouard, M., Pauty, F., *Compt. Rend.*, **252**, 514 (1961).
(3) Clark, R. P., *J. Chem. Eng. Data*, **18**, 67 (1973).
(4) Goodwin, H. M., Kalmus, H. T., *Phys. Rev.*, **28**, 1 (1909).
(5) Kelley, K. K., "Contributions to the Data on Theoretical Metallurgy XIII," U.S. Bureau of Mines, Bulletin 584, 1960.
(6) Mustajoki, A., *Ann. Acad. Sci. Fenn. Ser. A*, **VI**, No. 5 (1957).
(7) Sokolov, V. A., Shmidt, M. E., *Izv. Sekt. Fiz. Khim. Anal., Inst. Obshch. Neorg. Khim., Akad. Nauk SSSR*, **26**, 123 (1955).
(8) Sokolov, V. A., Shmidt, M. E., *ibid.*, **27**, 217 (1956).

Received for review September 19, 1973. Accepted April 12, 1975.

Thermal Conductivity of Anhydrous Borax, Boric Oxide, and Sodium Sulfate

Geoffrey K. Creffield[1] **and Anthony J. Wickens**
Borax Consolidated Ltd., Borax Research Centre, Cox Lane, Chessington, Surrey KT9 1SJ, England

The thermal conductivities of molten borax, boric oxide, and sodium sulfate are determined up to 1270K using the coaxial cylinders technique. The contribution owing to radiant transfer of heat is eliminated by extrapolating the observed results to zero sample thickness, and the true or molecular conductivities are described. In addition, the thermal conductivities of solid borax and boric oxide are determined between 318–553K and 310–503K, respectively, using a Lees' disc technique. The results are described.

The measurement of the thermal conductivity of molten borax, boric oxide, and sodium sulfate was conducted to provide much needed fundamental data for use in process heat transfer calculations: these three materials occur in the molten state in processes for the production of anhydrous borax and boric oxide. Data for borax and boric oxide in the solid state down to 298K were required to aid in the design of chill rolls by providing information necessary for heat transfer calculations.

Experimental

Solid products. The technique employed was based on the Lees' disc method in which the sample is held between two metal discs. Electrical power Q is supplied to one disc, and the temperature difference, ΔT, produced across the sample is measured. Under steady state conditions the thermal conductivity K can then be calculated from the equation

$$K = \frac{Qx}{A\Delta T} \tag{1}$$

where A is the area of the sample in contact with the heated disc, and x is the sample thickness.

In practice a twin plate system (*10*) was used. The apparatus consisted of two similar specimens (30 mm diameter, 5 mm thick) sandwiched vertically between a thin flat heater disc in the middle and two cold discs on the outside.

Heat losses from the edge of the heater (25 mm diameter, 6 mm thick), kept to a minimum by the use of insulation, were estimated in a separate experiment, and the thermal conductivity results were corrected to allow for this.

The cold sinks were made from solid blocks of aluminum (25 mm diameter, 12.5 mm thick) with thermocouple pockets (3 mm diameter) drilled to within 1 mm of the surfaces.

The sample discs of borax (Borax Consolidated Ltd., Special Quality grade) and boric oxide (prepared by dehydrating Special Quality grade boric acid supplied by Borax Consolidated Ltd.) were prepared by casting the molten salts into nickel moulds. The surfaces of the discs were ground flat using silicon carbide powder. When assembled, thin films of di-*n*-butylphthalate were applied to each side of the sample discs to improve thermal contact.

Power was supplied to the heater disc in small increments, and thermal equilibrium established each time before the temperature difference across each sample was recorded. After allowing for heat losses the conductivity was calculated using Equation 1.

Molten salts. An important source of error in all thermal conductivity measurements at high temperatures arises from the radiative transfer of heat, and this results in the observed conductivity being erroneously high. Gardon (*3*) has pointed out that failure to appreciate the radiation effect has been responsible for the wide variation in reported conductivity data for glasses and for values which appear to increase with sample thickness. Heat transferred per second by radiation is given by the Stefan-Boltzmann equation

$$Q_R = A\epsilon_{io}\sigma(t_i^4 - t_o^4) \tag{2}$$

where ϵ_{io} is a radiation interchange factor which involves the absorptivity and emissivity of the containers and the transmission coefficient of the sample. The latter is not always known for molten salt systems, and it is usually more beneficial to attempt to eliminate the radiation effect rather than calculate it.

For a liquid exhibiting radiant transfer of heat, the observed conductivity K_T may be considered (*2*) to be

---

[1] To whom correspondence should be addressed.

composed of two parts, molecular or true conductivity K_M and radiation transfer K_R. The total heat flux Q_T is the sum of the individual components for molecular conduction Q_M and radiation Q_R. Thus,

$$Q_T = Q_M + Q_R = \frac{K_M A (t_i - t_o)}{(r_o - r_i)} + \sigma A \epsilon_{io} (t_i^4 - t_o^4)$$

which rearranges to

$$\frac{Q_T (r_o - r_i)}{A (t_i - t_o)} = K_M + \sigma \epsilon_{io} \frac{(t_i^4 - t_o^4)(r_o - r_i)}{(t_i - t_o)}$$

Hence,

$$K_T = K_M + \sigma \epsilon_{io} \frac{(t_i^4 - t_o^4)(r_o - r_i)}{(t_i - t_o)}$$

where

$$\sigma \epsilon_{io} \frac{(t_i^4 - t_o^4)(r_o - r_i)}{(t_i - t_o)} = K_R$$

the equivalent conductivity for radiation. For small temperature differences the expression simplifies to

$$K_T = K_M + 4\, T^3 \sigma \epsilon_{io} (r_o - r_i) \qquad (3)$$

Thus, if the observed total conductivity is plotted as a function of sample thickness, the intercept at zero thickness will be the true or molecular conductivity K_M, and the contribution owing to radiation will have been eliminated.

The apparatus consisted of two coaxial cylinders constructed from platinum–10% iridium alloy. By using a series of outer cylinders, the sample thickness was varied from 1 to 5 mm.

Heat, generated by means of an electrical heater placed in the center of the inner cylinder, was conducted radially outward through the fluid-filled annulus to the outer cylinder. When thermal equilibrium had been established, the resulting temperature difference between the surfaces of the inner and outer cylinders $(t_i - t_o)$ was measured using Pt–Pt 13% Rh thermocouples and the thermal conductivity (K) calculated from the equation

$$K = \frac{Q \ln r_o/r_i}{2 \pi l (t_i - t_o)} \qquad (4)$$

where r_o and r_i are the radii of the outer and inner cylinders, l is the length of the main heater, and Q the power supplied to the heater.

This procedure was then repeated for increasing power input and at different overall temperatures for samples between 1 and 5 mm thick.

Heat losses in the axial direction were eliminated by two guard heaters placed above and below the main heater. Heat transfer by convection would also lead to erroneous results, and care was taken to ensure that the combination of the parameters' viscosity, sample thickness, and temperature difference was such that the product of the Grashof and Prandtl numbers did not exceed 1000, which Kraussold (7) established as being the threshold value for convective flow.

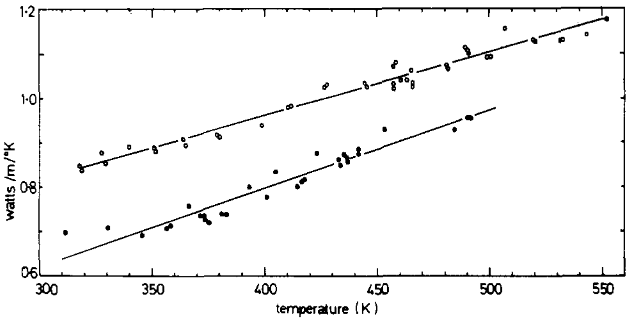

Figure 1. Thermal conductivity of borax and boric oxide in solid state

○ Borax
● Boric oxide

Results

Solid products. The thermal conductivities of borax and boric oxide are shown as functions of temperature in Figure 1. The experimental values have been deposited with the ACS Microfilm Depository Service. In the temperature range studied, the conductivities of both compounds are linearly dependent on temperature, and least-squares calculations give the respective equations as:

Borax (318–553K) $K = 0.40 + 0.0014\, T$
Boric oxide (310–503K) $K = 0.092 + 0.0018\, T$

where K is in watts $m^{-1}\, K^{-1}$, and T is in degrees Kelvin.

The present results for B_2O_3 are moderately higher than those of Lezhenin et al. (8) who reported values between 0.6 and 0.8 watts $m^{-1}\, K^{-1}$ in the range 373–673K. It is interesting to note that the present results are of the same order as the published data on pyrex (6) and other borate glasses (5).

Errors arising from the measurement of the geometry of the system are minimal ($<1\%$), similarly with the power input measurement. By far the greatest error occurred in the measurement of the temperature difference across the sample, but the accuracy was better than ±0.50K. This magnitude of error would result in a 3% error in the thermal conductivity of B_2O_3 at 343K, decreasing to 1.5% above 473K as the thermal gradient across the sample increased. The corresponding figures for borax are slightly higher, and at 343K the error is about 4%. The small temperature difference for borax at 318K resulted in a much larger error (up to 10%) which is reflected by increased experimental scatter at these lower temperatures.

Molten salts. The thermal conductivities of borax and boric oxide were measured between 570 and 1270K using samples 2, 3, 4, and 5 mm thick. In all cases, the conductivity increased smoothly with temperature and sample thickness. In addition, the temperature dependence appeared to be much greater at higher temperatures and for thicker samples. It is believed that these are the effects of radiation. When the observed conductivity (K_T) was plotted as a function of sample thickness $(r_o - r_i)$, a linear relationship was obtained for each compound, and by extrapolating these curves to zero thickness, the radiation effect was eliminated and the true or molecular conductivity (K_M) was obtained in accordance with Equation 3. Molecular conductivities calculated in this manner are shown in Figure 2 as functions of temperature. The numerical data have been deposited with the ACS Microfilm Depository Service.

For boric oxide the true conductivity increases linearly between 620 and 1270K and is best represented by the equation

$$K_M = 0.237 + 0.0011\, T$$

where K_M is in $W\, m^{-1}\, K^{-1}$, and T is in degrees Kelvin.

The results for borax show an upward curvature at higher temperatures and between 570 and 1270K are best described by the equation

$$K_M = 4.096 - 0.125 \times 10^{-1}\, T + 0.150 \times 10^{-4}\, T^2 - 0.462 \times 10^{-8}\, T^3$$

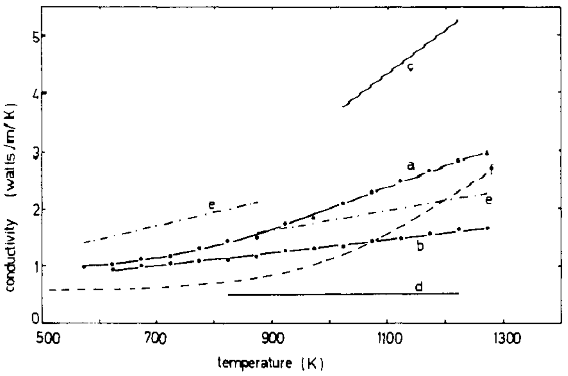

Figure 2. Comparison of reported thermal conductivities of molten borax and boric oxide
a: Borax (this determination)
b: Boric oxide (this determination)
c: Borax [Gutman et al. (4)]
d: Boric oxide [Ewing et al. (2)]
e: Boric oxide [Nishimura et al. (9)]
f: Boric oxide [Lezhenin et al. (8)]

The present results are compared with the work of previous authors in Figure 2. Only one reference exists on the thermal conductivity of molten borax (*4*), and these results are much higher than those presently reported. The temperature dependence of these results is also higher; this suggests the possibility of some radiative heat transfer to which the authors made no reference.

Three reports exist concerning measurements on liquid boric oxide. Ewing et al. (*2*) described the thermal conductivity between 773 and 1173K. To eliminate the contribution owing to radiation, they measured the apparent thermal conductivity at a series of temperature differences and extrapolated their results to $\Delta T = 0$. By this method they showed that the true or molecular thermal conductivity was constant ($=0.54$ W m^{-1} K^{-1}) over this temperature range. [They claimed that this was to be expected for fused inorganic compounds, part of this claim being based on the fact that the velocity of sound waves (phonons) is independent of temperature. However, the velocity of sound in B_2O_3 does increase with temperature (*1*).]

Nishimura et al. (*9*) presented three equations which cover the range 373–1273K. The method of presentation leads to discontinuities in the curves, but the temperature dependence is roughly the same as in the present results.

Lezhenin et al. (*8*) have recently published results which agree fairly well with our work up to about 1050K, but at higher temperatures the conductivity increases much more rapidly. This could well be the result of ignoring the increasing radiation effect.

A preliminary investigation of sodium sulfate has suggested similar behavior for the borates. The thermal conductivity was measured between 1160 and 1270K for two sample thicknesses, and again the radiation contribution was eliminated by extrapolating results to zero sample thickness. A linear dependence has been assumed in this case, although this not strictly valid, since the earlier experiments with borax and boric oxide, where more results were available, suggested the relationship was linear. The true (molecular) conductivity between 1160 and 1270K is best described by the equation

$$K_M = -30.04 + 9.063 \times 10^{-2} T - 9.154 \times 10^{-5} T^2 + 3.108 \times 10^{-8} T^3$$

where K is in W m^{-1} K^{-1}, and T is in degrees K. Numerical data have been deposited with the ACS Microfilm Depository Service.

By far the greatest source of error in the results for the molten salts lay in the measurement of the temperature difference between inner and outer cylinders. It has been estimated that the accuracy of these readings was ±0.05K. The resulting error in the value of the thermal conductivity depended on the magnitude of each individual temperature difference, but the average was generally ±5%. It was further estimated that the calculations to obtain the true conductivity, involving extrapolation to zero sample thickness, involved an error of ±6% which resulted in an overall error in the true conductivity of ±8%. This is an average figure, with results at lower temperatures being rather more accurate than this and vice versa at high temperature.

In the case of sodium sulfate, results were obtained at only two sample thicknesses; hence, the extrapolation process involved greater error than with the borates. An overall error of ±12% would probably be more realistic for this salt.

Literature Cited

(1) Bockris, J. O'M., Kojonen, E., *J. Am. Chem. Soc.*, **82**, 4493 (1960).
(2) Ewing, C. T., Spann, J. R., Miller, R. R., *J. Chem. Eng. Data*, **7**, 246–50 (1962).
(3) Gardon, R., *J. Am. Ceram. Soc.*, **44**, 305 (1961).
(4) Gutman, M. B., et al., *Electrotermiya. Nauk-Tekh. Sb.*, No. 57, 25–27 (1967).
(5) "Handbook of Chemistry and Physics," 54th ed., Chemical Rubber Publ., Cleveland, Ohio, 1973.
(6) Jakob, M., "Heat Transfer," Vol I, p 95, Wiley, New York, N.Y., 1949.
(7) Kraussold, H., *Forsch. Geb. Ingenieurwes.*, **5**, 186 (1934).
(8) Lezhenin, F. F., et al., *Teplofiz. Teplotekh.*, **25**, 94–96 (1973).
(9) Nishimura, M., et al., *Kagaku Kogaku*, **36** (6), 640–47 (1972).
(10) "Thermophysical Properties of Matter," Vol II, "Non-metallic Solids, Experimental Determination of Thermal Conductivity," Y. S. Touloukiau, Ed., p 16a, IFI/Plenum, New York-Washington, 1970.

Received for review February 4, 1974. Accepted March 11, 1975. Work sponsored by and published with the permission of U.S. Borax and Chemical Corp.

Supplementary Material Available. Experimental values and numerical data for smoothed equations will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JCED-75-223.