schen Atomen und Aggregaten spezifischer Größe. In dem in dieser Arbeit diskutierten ebenen Problem ist der Wirkungsquerschnitt die Summe der Durchmesser der Stoßpartner. Für die Berechnung des Durchmessers eines n-atomigen Aggregats muß in der betrachteten Näherung konsequenterweise die Summe der Projektionsflächen der den Keim bildenden Atome verwendet werden. Ist d der Einzelatomdurchmesser, so ergibt sich für den Wirkungsquerschnitt:

$$\sigma = d + d_n = (\sqrt{n} + 1)\, d\,. \tag{10}$$

Mit der Sprungweite des Atomplatzwechsels a und der Aktivierungsenergie für den Platzwechsel E_{P} erhält man für die Diffusionsgeschwindigkeit

$$v = (a/\tau_0)\, \exp\{-E_{\mathrm{P}}/k\,T\}\,. \tag{11}$$

Für die in die Beziehung für die Lebensdauer einzusetzende Zerfallskonstante ergibt sich also

$$K_n = \sigma\, v = a\, d\, (\sqrt{n} + 1)\, \frac{1}{\tau_0} \exp\left\{-\frac{E_{\mathrm{P}}}{k\,T}\right\}. \tag{12}$$

Herrn Prof. Dr. H. Raether danke ich für das fördernde Interesse an dieser Arbeit.

Thermal Expansion of Lithium Sulphate

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The coefficient of linear thermal expansion has been measured for polycrystalline Li_2SO_4. Between 200 and 550 °C (monoclinic phase) the average linear coefficient of thermal expansion was determined to $(22 \pm 1) \times 10^{-6}$ degr.$^{-1}$, and for the range 600—750 °C (cubic phase) the coefficient $(43 \pm 3) \times 10^{-6}$ degr.$^{-1}$ was obtained. The quoted errors are standard deviations.

The volume change at the transition between the monoclinic and cubic phases was found to be 2.2 cm^3/mole, which is in good agreement with Pistorius' estimation from the pressure-temperature curve of this transition.

In connection with other investigations of lithium sulphate performed in this laboratory a simple equipment has been constructed for measuring the thermal expansion of the salt[1]. A rough estimation of thermal expansion is often desired when constructing experimental equipment, as well as for interpreting other measurements. Thus, when discussing transport mechanisms for diffusion and electrical conduction of Li_2SO_4 between 600 and 800 °C the activation energy of equivalent conductivity has recently been estimated by Kvist[2], under the assumption that the thermal expansion is negligible. The density was taken as 2.08 g cm^{-3} at all temperatures.

Experimental

In all experiments reagent grade lithium sulphate was used without further purification. The salt was melted in a platinum mould, which gave a square salt column of about 45 mm length after solidification. The sample was placed in a quartz tube with a flat bottom and a diameter of about 20 mm. Another quartz tube with a flat bottom was placed on top of the salt specimen and a Chromel-Alumel thermocouple was used for measuring the temperature at the middle of the sample. The tubes were placed in the center of a vertical tube furnace. The arrangement is shown in Fig. 1. A holder with a universal transducing cell with a linear displacement accessory (Statham Model UC 3) was fixed on top of the outer tube. The holder could be adjusted to the inner tube and the expansion of the sample was then registered by a recorder (Philips PR 2500). The temperature was measured at intervals with a d. c. potentiometer (Croydon Type P 3). The measurements were usually performed with a temperature change of about five degrees per hour. The thermal expansion (ΔL) divided with the room temperature length (L) of the salt column was plotted against the corresponding temperature in a diagram. The coefficient of thermal expansion taken from the diagram was then corrected for the expansion of the outer quartz tube, for which a coefficient of $0.55 \cdot 10^{-6}$ deg.$^{-1}$ was used[3].

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[1] For a survey of methods see e. g. P. Hidnert and W. Souder, Nat. Bur. Standards (US) Circ. 486 [1950].

[2] A. Kvist and U. Trolle, Z. Naturforsch. **22 a**, 213 [1967].

[3] Handbook of Chemistry and Physics Ed. 41 p. 2243, Chemical Rubber Publishing Company, Cleveland, Ohio, 1959.

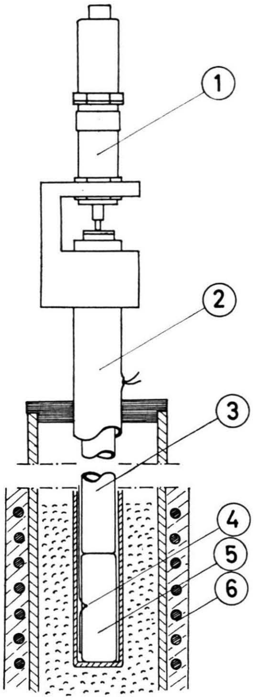

Fig. 1. Arrangement for measuring the coefficient of thermal expansion for Li_2SO_4. 1. Transducing cell with linear displacement accessory. 2. Outer quartz tube. 3. Inner quartz tube. 4. Thermocouple. 5. Salt sample. 6. Heating coil.

In a furnace of our type a slight radial temperature gradient might be expected. The heat production is in the cylindrical coil, and the heat loss is mainly upwards in the axial direction. The result should be that the temperature at a horizontal level is lowest at the axis, which should be the case both while the oven is heated and while it is cooling off. In order to check this possible source of error, measurements were made also with a quartz sample, and it was found for both increasing and decreasing temperatures, that the inner tube had expanded slightly less than the outer one. A correction term was estimated, and it was found to be negligible for our measurements on lithium sulphate.

Results and Discussion

The equipment was checked by measuring a copper sample. For temperatures between 200 °C and 500 °C the measurements gave a value of $(17.6 \pm 0.7) \cdot 10^{-6}\ \text{deg}^{-1}$ for the coefficient of linear thermal expansion, which is in good agreement with available data in the literature[4]. The error given here is an estimated value from the technical data of the equipment involved. All our measurement on copper gave values within these limits. (For the lithium sulphate results below, the standard deviation is instead quoted.)

Lithium sulphate has a phase transition at about 570 °C, above which a face-centered cubic modification with unusual rheological and electric properties is obtained. This is of importance for the present experiments. Thus, in contrast to the measurement on copper, the mode of temperature change was critical for the apparent volumle change of lithium sulphate. In some prelusive experiments where the temperature was increased at a rate of 5 – 10 degr./min, the results were obviously not reliable. When the temperature was increased slowly (5 – 10 degr./hour) the thermal expansion above the transition point was still not reproducible from sample to sample, or between repeated measurements on the same sample. This is probably due to a slight deformation of the sample under the load of the inner quartz tube, cf the viscous properties of fcc lithium sulphate[5]. However, for decreasing temperatures, the thermal contraction was always reproducible (and slightly larger than the aparent expansion measured when the sample was heated). A typical length vs temperature curve is shown in Fig. 2.

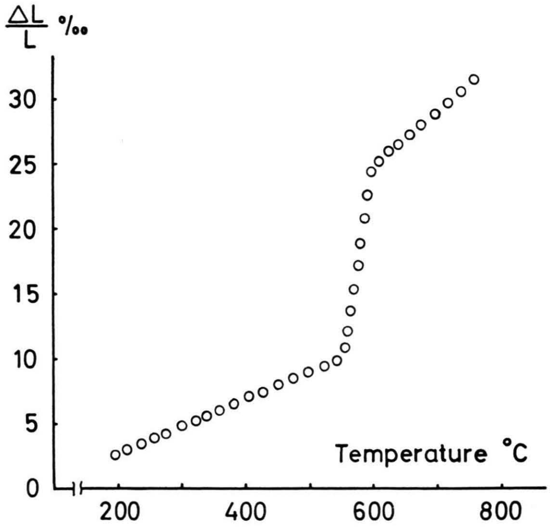

Fig. 2. Thermal expansion curve for Li_2SO_4.

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[4] P. Hidnert, Sci. Pap. NBS **17**, 91 [1922].

[5] B. Augustsson and A. Lundén, Z. Naturforsch. **21 a**, 1860 [1966].

For polycrystalline monoclinic lithium sulphate a constant coefficient of thermal expansion, $(22 \pm 1) \times 10^{-6}$ degr.$^{-1}$, is obtained over the range $200 - 550$ °C, and it appears as if the coefficient might be slightly lower in the region between 200 °C and room temperature. The thermal expansion of monoclinic lithium sulphate has been estimated previously by Pistorius [6], who measured the powder diffraction pattern at 500 °C. From a comparison with the somewhat inaccurate room-temperature values of the unit-cell constants, he concluded that the thermal expansion takes place mainly along the c-axis. The difference between the quoted unit cell volumes at 500 °C and room temperature corresponds to an average coefficient of (linear) thermal expansion of 39×10^{-6} degr.$^{-1}$, which is higher than our result given above.

For cubic lithium sulphate the contraction measurements give a coefficient of thermal expansion of $(43 \pm 3) \times 10^{-6}$ degr.$^{-1}$ for the range $600 - 750$ °C. This coefficient of thermal expansion can be used to recalculate the above mentioned activation energy of the equivalent conductivity. For the entity ΛT (product of conductivity and absolute temperature) the activation energy is now obtained as

$$Q_{\Lambda T} = 10\,360 \pm 700 \text{ cal/equiv.},$$

which is about 2% higher than the published value [2].

From the present experiments the volume change at the transition point is estimated to 4.2%. This corresponds to a volume change,

$$\Delta V_{\text{tr}} = 2.2 \text{ cm}^3\text{/mole}.$$

This result is in good agreement with the volume change Pistorius calculates from the pressure-temperature curve and the heat of reaction by applying the Clausius-Clapeyron relation (2.2 ± 1 cm^3/mole), while the obtains 0.9 ± 0.6 cm^3/mole from the unit cell volumes measured by high-temperature X-ray diffractometry [6].

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[6] C. W. F. T. Pistorius, Z. Phys. Chem. NF **28**, 262 [1961].

A Plane Source Method for Measuring Interdiffusion Coefficients of Transparent Liquids

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A bottom layer diffusion technique is described, where an experiment is initiated by dropping a crystal of the diffusing substance to the bottom of a properly designed container for the liquid. It is shown that this technique is comparable to any other method from point of view of accuracy while the experimental procedure is extremely simple. The technique is tested at room temperature on two aqueous solutions with widely different diffusion coefficients. It is also applied to the determination of the interdiffusion coefficient of the silver ion in the three molten salts: sodium, potassium, and rubidium nitrate.

Optical methods have proved to be very useful in the study of liquid diffusion at room temperature because of their accuracy and the possibility to follow the process for a long period of time. The great amount of information which can be obtained from one particular experiment contributes to an important check of the internal consistency of the data which is necessary if the presence of convective motions in the liquid is to be ruled out. Since the problem of using optical techniques at high temperatures has been solved [1, 2], it seems to be a rather straightforward application to measure interdiffusion coefficients of transparent liquids. This would, however, be a very difficult technical problem if one would try to use any of the conventional "draw-slide", "sliding-solvent", or "flowing-junction" cells in order to approximate the initial condition of a sharp interface in an infinite medium [3]. A procedure which ought to be more attractive is the one described by Ljunggren and Lamm [4] who injected a concentrated

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[1] L. W. Wendelöv, L.-E. Wallin, and S. E. Gustafsson, Z. Naturforsch. **22 a**, 1180 [1967].

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

[3] O. Bryngdahl, Acta Chem. Scand. **12**, 684 [1958].

[4] S. Ljunggren and O. Lamm, Acta Chem. Scand. **11**, 340 [1957].