keit der Ladungsträger, homogene und isotrope Turbulenz etc.) zu beseitigen. Die Erweiterung auf Störstellenleitung und verschiedene Beweglichkeiten führt, selbst wenn die Trägerdichten sehr verschieden sind, zu keinen prinzipiellen Schwierigkeiten. Sie bringt jedoch eine Vergrößerung des rechnerischen Aufwandes mit sich.

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Plastic Flow of Solid Mixtures of Li_2SO_4 and K_2SO_4

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The addition of K_2SO_4 to Li_2SO_4 causes a considerable change in the rheological properties of the cubic high temperature modification. A simple device for relative measurements of the plastic flow of the salt consisted of a sphere of stainless steel at the end of a steel rod on top of which weights were hung in order to obtain a suitable penetration rate through the salt. This rate depended on the composition of the mixture as well as on the thermal pretreatment of the salt. The temperature dependence was strong; a crude estimation gave an "activation energy" of the order of 2×10^5 cal/mole, i. e. more than an order of magnitude higher than for electrical conductivity or cation self-diffusion. This result is in agreement with the interpretation of the electrical conductivity as being due solely to cation transport.

In a recent investigation of electromigration in lithium-rich solid mixtures of alkali sulfates it was found that the electrodes sunk down into the salt[1], while this did not occur for pure α-Li_2SO_4. From this observation we concluded that it should be possible to make crude measurements of the "viscosity" of the solid mixtures and compare the results with self-diffusion and conductivity data.

The measuring device consisted of a sphere of stainless steel (diam. 20 mm) sitting at the low end of a steel tube (ext. diam. 6 mm), which was centered through an opening in the top lid of a vertical steel tube (inner diameter 58 mm) containing the salt. The wide tube was heated in an oven, where the temperature gradient was negligible over a range of several cm. The temperature was measured with a thermocouple (MegopaK type K, Honeywell Regulator Company) placed inside the steel sphere. By loading weights on top of the 6 mm tube, the sphere was forced to penetrate through the salt with a rate that was measured with a cathetometer. Pure Li_2SO_4 and four mixtures were investigated, see Table 1.

In the experiments with 0, 4.0, 8.5, and 12.4% K_2SO_4 the salt was first heated to about 900 °C and then cooled to the desired temperature. When this temperature became stable, the sphere was lowered until it touched the surface of the salt, and the measurement was started. The penetration rate which was highest in the beginning became constant after a depth of the order of the radius of the sphere had been reached. However, in some cases the penetra-

K_2SO_4 mole %	Temp. °C	v mm/h	Remark
0	780	$\ll 0.1$	h, e
4.0	732	5.9	h
	680	0.1	h, e
	630	0.01	h, e
8.5	620	2.1	h
	605	1.4	h
12.4	580	23	h
	570	0.5	h, e
0.86	825	51	h
	820	27	h
	815	1.6	h
	820	2.1	c
	810	0.79	c
	805	0.73	c

Table 1. Penetration of a heavy steel device through solid $Li_2SO_4-K_2SO_4$ mixtures[3]. v = constant penetration rate. The thermal pretreatment is indicated by h if the desired temperature was approached from above, and by c if from below. e denotes that the sphere had penetrated only slightly into the salt, and that the extrapolated v is only to be taken as an approximate indication of the order of magnitude.

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[1] V. LJUBIMOV and A. LUNDÉN, Z. Naturforschg., in press.

tion was too slow for this depth to be reached within some 10 hours and an assumed constant rate v was extrapolated by a comparison of the times at which depths of e. g. 1 or 2 mm were reached in different experiments. These estimated rates, denoted by e in Table 1, are considered to, at best, indicate the right order of magnitude. For the mixtures with 0.86% K_2SO_4 the sphere was placed at a fixed position, about 5 cm below the surface of the salt, before the measurement started. Also in this case it usually took some time before the velocity v became constant. As before, the salt was heated to about 900 °C between two measurements. The cooling was either stopped at the chosen temperature or continued to about 650 °C, after which the salt was heated slowly to the temperature at which we were going to measure. (This latter procedure is indicated by c in Table 1, whilst h stands for the simpler procedure.) The choice of thermal pretreatment has a drastic effect on the penetration rate.

Stainless steel corrodes slightly in sulfate melts, and we noticed that the salt gradually became miscoloured. However, when a salt sample was dissolved in water, neither Fe^{2+} nor Fe^{3+} ions were detected, and the amount of insoluble impurities was small. Thus we concluded that the possible contribution from undesired impurities to the observed changes in plastic flow should be negligible.

According to BERGMAN et al.[2] the melting point decreases from 860 to 535 °C when going from 0 to 20% K_2SO_4. There is thus a considerable temperature range that was not covered by the present measurements, except for the observation that the device we used penetrated too fast through the solid salt to permit measurements. Of course it would have been possible to extend the measurements to higher temperatures by reducing the load on top of the tube, but for the present comparison we preferred to have the same weight in all measurements.

Although the present measurements cannot be considered as accurate[3], they prove that the plastic flow depends strongly on composition, temperature, and the pretreatment of the salt. For a comparison with liquids it is instructive to estimate the "viscosity" of the salt by applying STOKE's law. If we thus consider the total weight of the sphere, supporting tube and load (788.65 grams) as the force acting on a sphere of radius 1.0 mm, we obtain $\eta = 1.48 \times 10^9 \, v^{-1}$ poise, if the velocity v is in mm/h as in Table 1. The highest rate measured by us (0.86%, 825°) will then correspond to a "viscosity" of 3×10^7 poise. The calculation is of course very simplified, since we have neglected i. a. the friction between the 6 mm tube and the salt[4]. Nor have we made any correction for the influence of the container wall, as is usually done in viscosimetry[5]. Viscosity in liquids, as well as conductivity and self-diffusion in both liquids and solids, is often considered as a process governed by an activation energy Q. If we assume that the measured penetration rate is inversely proportional to a "viscosity", the usual expression $\eta = \eta_0 \exp\{Q/(R\,T)\}$ might be transformed to $v = v_0 \exp\{-Q/(R\,T)\}$, where v is the penetration rate measured at the temperature T and R is the gas constant. If we restrict our calculations to the 0.86% mixture, the measurements on "cooled" salt (c in Table 1) give an activation energy of about 1×10^5 cal/mole, while the other measurements correspond to at least 3×10^5 cal/mole. Although an estimated activation energy of the order of 2×10^5 cal/mole might be characteristic only for mixtures of approximately this composition at about 820 °C, it can be used for a comparison with the activation energies of the order of 10^4 cal/mole found for the electrical conductivity and cation self-diffusion of pure lithium sulfate[6]. For liquids the activation energies of the three transport processes usually are of the same order of magnitude, which we thus find is not the case for the solid sulfates. This result is in agreement with our current model according to which the cations have a high mobility in a lattice built up by the sulfate ions. While the high electrical conductivity is mainly due to cation mobility, plastic flow requires a deformation of the anion lattice, which should correspond to a much larger activation energy.

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[2] A. G. BERGMAN, A. I. KISLOVA, and V. I. POSYPIAKO, Dokl. Akad. Nauk USSR **88**, 815 [1953].

[3] The results for the 0.86% mixture are to be considered as more reliable than for the other series, since several improvements were made in the experimental techniques before the last mixture was studied. However, even the first measurements are sufficient as a base of a qualitative discussion.

[4] The neglected tube surface is about 75% of the surface of the sphere, when the penetration has gone so far that 5 cm tube length is surrounded by salt. The gradual increase in total surface area (sphere + tube) was of the order of 10% for several of the measurements reported here.

[5] A. DINSDALE and F. MOORE, Viscosity and its Measurement, Chapman and Hall, London 1962.

[6] A. KVIST and A. LUNDÉN, Z. Naturforschg. **20 a**, 235 [1965].