In the equimolar mixtures, the conductivity mainly depends on the heavier cation. This can be explained by assuming some sort of cooperative motions in the salt[5], where a light cation, for instance a lithium ion in thallium sulphate, moves with the same velocity as the thallium ions. A result of this is that the conductivity of $TlMeSO_4$ almost is the same for all Me (Fig. 1). For $LiMeSO_4$ the situation is reversed (Fig. 2). It can also be observed that in the mixture $Tl_2SO_4 - Rb_2SO_4$ and in other mixtures, where the cation radii are narly equal, both Λ and Q are ideal. This has been observed also for nitrates[17]. A comparison between Table 6 and 7 shows that when we mix two salts with very different cation radii, we obtain a very large positive excess activation energy and a negative excess conductivity. This is in agreement with the model mentioned above, since the free volume of a sulphate increases with the radius of the cation[5].

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Diffusion in Cubic Sulphates

I. Univalent Cations in Pure Lithium Sulphate

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The interdiffusion coefficients (D) of Na^+, Ag^+, K^+, Rb^+ and Tl^+ in pure f. c. c. Li_2SO_4 have been measured between 590 and 820 °C. D and the Arrhenius' activation energies decrease in the same order as the ionic radii increase. D is a function both of the masses and the radii of the impurity cations. The results show that the Na^+ and Ag^+ ions mainly diffuse in the sulphate lattice with the same mechanism as the lithium ions, while the larger ions are mobile in defects in the lattice. The Li^+, Na^+ and Ag^+ ions are probably diffusing between octahedral positions.

Some salts form cubic high temperature modifications with extremely high mobility of the cations. Such modifications can be found in e. g. AgI (l. c. [1-2]), Li_2SO_4 (l. c. [3-5]), $LiAgSO_4$ (l. c. [6-7]) and $LiNaSO_4$ (l. c. [7-8]). During the last years we have made a great number of investigations of especially lithium sulphate and we have now started a serie of measurements of different diffusion coefficients in cubic sulphates. We report here on measurements of the interdiffusion coefficients of the univalent cations Na^+, Ag^+, K^+, Tl^+ and Rb^+ in f. c. c. Li_2SO_4. The self-diffusion coefficient of lithium in this modification has recently been published[4] and measurements of thermal diffusion coefficients have also been reported[8-9].

Experimental

All salts were of reagent quality and were used without further purification. The diffusion cells were made of pure quartz (Fig. 1) and all measurements were performed in air. Pure lithium sulphate was molten in the bottom of the tube, which was placed in a big furnace. When the salt had solidified to an about 70 mm long column and the experimental temperature was reached, we inserted a funnel, which contained a few small lumps of lithium sulphate with 2 – 3 mole% of the impurity cation. The salt in the funnel was molten by means of a small winding around the tube and in this way an about 0.5 mm thick layer of salt containing impurities was obtained on the surface of the salt column. The cell was then held at constant temperature for 3 – 8 hours, when it was rapidly cooled to room temperature. Samples were taken at every fourth mm of the salt column, and were analysed by means of flame spectrophotometry.

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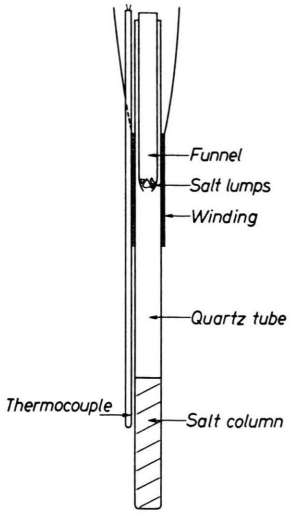

Fig. 1. The diffusion cell.

Results

The salt column can in this case be considered as semi-infinite and since the thickness of the surface layer is small, we get

$$c = c_0 \cdot \exp(-x^2/4\,D\,t),$$

where c_0 is the concentration of the diffusion ion in the surface layer at the time t. x is the distance from the surface and D the diffusion coefficient.

If we plot $\log c$ as a function of x^2, D is easily obtained from the slope of a straight line. Fig. 2 shows the results for a typical diffusion experiment. For all runs with Na^+ and Ag^+ the deviation from a straight line was small, but in some experiments with K^+, Tl^+ and especially Rb^+ no diffusion coefficients could be calculated due to a definite positive curvature. It was also more difficult to make accurate chemical analysis of the rubidium samples. With our actual equipment for chemical analysis it was also impossible to investigate caesium diffusion.

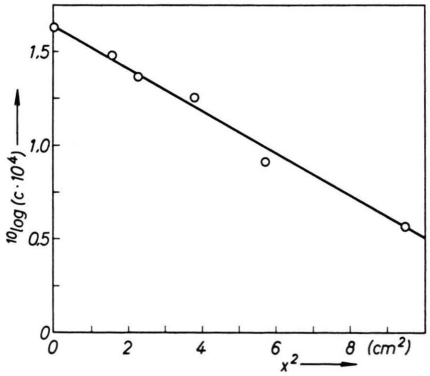

Fig. 2. Results for a typical diffusion experiment. c is the concentration in mole% and x the distance from the surface of the salt column.

The obtained diffusion coefficients are tabulated in Table 1. The temperature dependence of D can be described by an Arrhenius equation

$$D = D_0 \cdot \exp(-Q/R\,T),$$

where R is the gas constant and T the temperature in °K. Fig. 3 shows $^{10}\log D$ as a function of $1/T$ and in Table 2, we have tabulated D_0 and Q. The standard deviation of D is about 3%. The self-diffusion coefficient for the lithium ion is also given for comparison [4].

Ion	t °C	D cm²/s	time min
Na	604	2.02	380
	613	2.15	388
	693	3.10	314
	791	4.25	196
	820	4.64	300
Ag	595	1.53	518
	672	2.12	285
	687	2.11	398
	792	3.11	362
	806	3.44	180
K	595	1.39	430
	646	1.58	496
	692	2.04	345
	810	2.39	199
	812	2.24	995
Rb	624	1.03	624
	722	1.13	722
	794	1.20	794
Tl	621	1.33	326
	673	1.46	360
	732	1.64	365
	797	2.03	318

Table 1. The interdiffusion coefficients of Na^+, Ag^+, K^+, Rb^+ and Tl^+ in f.c.c. Li_2SO_4.

Ion	$D_0 \cdot 10^5$ cm²/s	Q cal/mole	s_Q cal/mole	s_D cm²/s	$D_{750} \cdot 10^5$ cm²/s
Li	206.3	7930	890	0.24	4.16
Na	132.5	7250	200	0.05	3.73
Ag	86.0	6970	340	0.09	2.78
K	18.0	4380	610	0.13	2.09
Tl	16.0	4460	770	0.06	1.78
Rb	2.7	1740	10	0.01	1.16

Table 2. The diffusion coefficients described by $D = D_0 \cdot \exp(-Q/R\,T)$, where R is the gas constant, T the temperature in °K and s the standard deviations. The values for lithium sulphate were obtained from a previous paper [4].

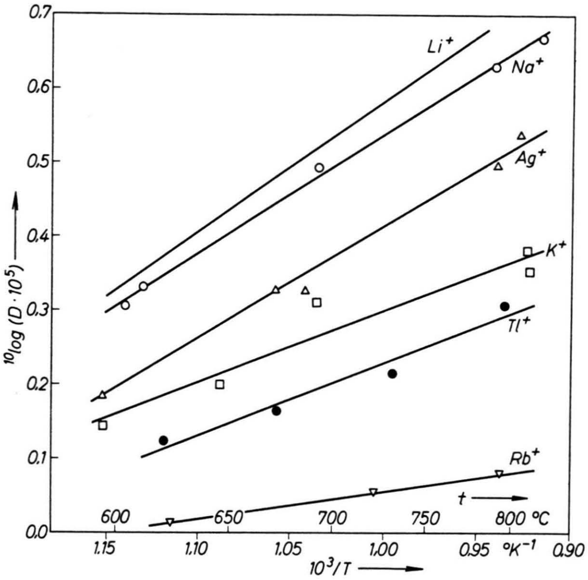

Fig. 3. $^{10}\log D$ as a function of $1/T$, where D is the diffusion coefficient and T the temperature in °K.

Discussion

In the sulphate lattice there are tetrahedral and octahedral positions available for the cations, and the lithium ions are probably mainly distributed over the tetrahedral positions [5, 7]. Lithium ions in octahedral positions can then be considered as thermal defects. The sodium and silver ions, and perhaps also the potassium ions should be small enough for the octahedral positions, but too large for the tetrahedral positions. The rubidium and thallium ions are too large for both positions.

D decreases in the order Li^+, Na^+, Ag^+, K^+, Tl^+ and Rb^+. For all cations the diffusion coefficients are very high compared with ordinary solids, i. e. also for the rubidium and thallium ions. Although D decrease in the same order as the ionic radii increase, there is also a mass dependence, and $D(Tl^+)$ is much greater than $D(Rb^+)$ in spite of the equality in Pauling radii of the two ions.

However, since it is possible to find a physical meaning of Q and D_0, it is more interesting to compare these quantities instead of D. The two smallest impurity cations, Na^+ and Ag^+, have activation energies, which are only a little smaller than for self-diffusion and it seems thus plausible to assume that we have the same mechanism of transport for these three ions. On the other hand comparably low Q values were obtained for K^+, Tl^+ and Rb^+ diffusion. D_0 is also comparably lower for these ions.

From measurements of electrical conductivity and diffusion in pure f. c. c. Li_2SO_4, we have found it probable that we have different mechanisms of transport for diffusive and electrical mobility [4]. Electromigration and conductivity measurements have shown that there are cooperative motions of ions in the salt and that approximately two cations take part in a jump [5]. This mechanism should not be valid for diffusion. For diffusion we have assumed that we might have some sort of ring mechanism, which leads to a smaller activation energy for diffusion than for electrical conduction.

Further conclusions about the transport mechanism in f. c. c. Li_2SO_4 can now be drawn from the interdiffusion results. The sodium and silver ions evidently diffuse with the same mechanism as the lithium ions and since the sodium and silver ions are too large for the tetrahedral positions, the diffusion must take place between octahedral positions. This should then also be valid for self-diffusion and is in disagreement with our previous model with a pure ring mechanism.

If the jump lengths for Li^+, Na^+ and Ag^+ are identical, which seems probable, D_0 should be proportional to the vibration frequency (ν) of the ion, and ν is proportional to the inverse root of the reduced mass of the ion (m_{red}), where m_{red} is given by the relation

$$m_{\text{red}} = (m_0 + m')\, m'' / (m_0 + m' + m'') .$$

m_0 is the mass of the ion, m′ the mass vibrating in phase with m_0 and m'' the mass vibrating in counterphase to m_0.

Nothing is, however, known about the magnitude of m' and m'' for diffusion in f. c. c. Li_2SO_4. But if we consider D_0 as a function of $m_0^{-\frac{1}{2}}$, the product $D_0\, m_0^{\frac{1}{2}}$ (Table 3) indicates that the mass vibrating

Ion	$D_0 \cdot 10^5$ cm²/s	$m_0^{\frac{1}{2}}$	$D_0\, m_0^{\frac{1}{2}} \cdot 10^5$
Li	206.3	2.63	543
Na	132.3	4.80	635
Ag	86.0	10.38	894
K	18.0	6.25	112
Tl	16.0	14.30	229
Rb	2.7	9.25	25

Table 3. The product $D_0^{\frac{1}{2}}$ for the different cations. m_0 is the mass of the cation in mass units.

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.

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Optical Determination of Thermal Conductivity with a Plane Source Technique

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

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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

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