Diffusion in Cubic Sulphates

III. Divalent Cations in Pure Lithium Sulphate

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The diffusion coefficients of the divalent ions Mg, Zn, Ca, Cd and Pb have been measured between 600 and 800 °C. The results can be described by an Arrhenius equation, where the pre-exponential factors decreases when the radius of the diffusing ion increases. By comparing results for univalent and divalent ions we have found that the formation energy is constant and that the migration energy decreases when the cation radius increases.

We reported recently on diffusion of univalent cations in cubic lithium sulphate[1]. Since we wanted to obtain more complete information about the transport mechanism in this salt, we have now studied diffusion of the divalent ions Mg, Zn, Ca, Cd and Pb and also tried to investigate Mn, Ba and Be diffusion.

The experimental technique has been described previously[1]. The results for Ba^{++} and Mn^{++} are only of qualitative nature due to difficulties with the chemical analysis, while for Be^{++} we only found that the diffusion coefficient is very small.

The results are given in Table 1 and Fig. 1. The diffusion coefficients are for all ions much greater than in "ordinary" solids. For instance for lithium sulphate at room temperature the diffusion coefficient is only about $0.5 \cdot 10^{-11}$ cm²/s (l. c. [2]).

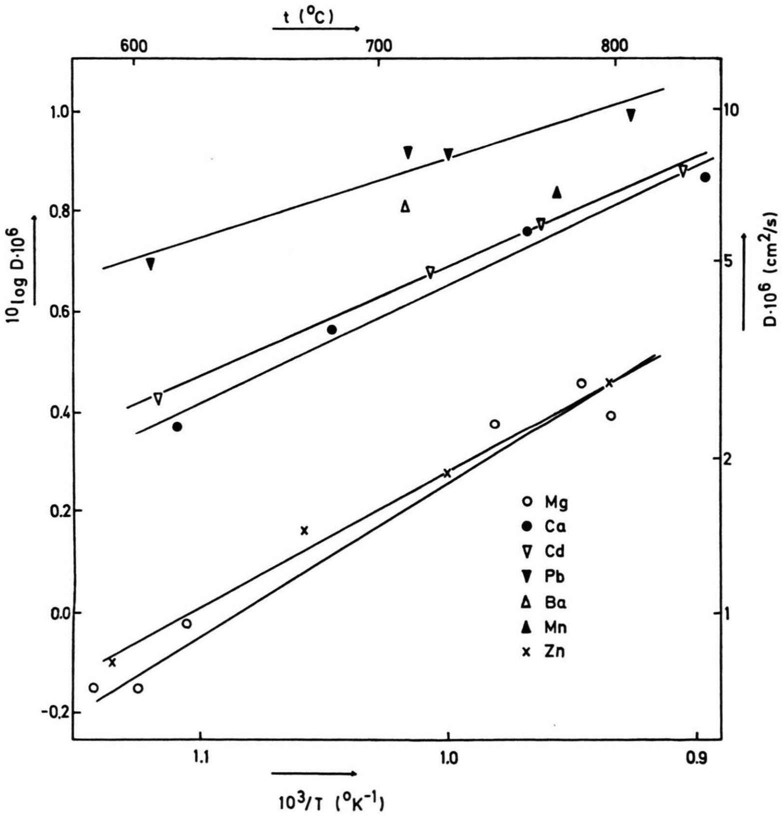

Fig. 1. The diffusion coefficients of divalent cations in cubic lithium sulphate.

Ion	t °C	$D \cdot 10^5$ cm²/s	time min
Cd	623	0.267	1305
	720	0.477	985
	766	0.597	640
	832	0,762	385
Ca	629	0.236	972
	682	0.366	395
	760	0.575	985
	843	0.738	1317
Mg	603	0.0706	2643
	617	0.0704	4120
	632	0.0947	2388
	746	0.237	3685
	784	0.286	1400
	798	0.248	1192
Zn	607	0.0790	1260
	672	0.145	2555
	728	0.189	985
	797	0.288	2553
Pb	621	0.493	324
	711	0.823	352
	728	0.820	475
	807	0.986	366
Mn	773	0.688	347
Ba	710	0.642	516

Table 1. The interdiffusion coefficients of Cd^{++}, Ca^{++}, Mg^{++}, Zn^{++}, Pb^{++}, Mn^{++} and Ba^{++} in f.c.c. Li_2SO_4.

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[1] A. Kvist and A. Bengtzelius, Z. Naturforsch. **23 a**, 679 [1968].

[2] E. D. Kuznets and L. M. Yakimenko, Zh. Prikl. Khim. **40**, 786 [1967].

D increases for the divalent ions, but decreases for the univalent ions when the ionic radii increase (Fig. 2), but if D is described by an Arrhenius equation, $D = D_0 \exp(-Q/R\,\mathrm{T})$, it is found that D_0 and Q decrease, when the ionic radii increase both for the univalent[1] and divalent cations (Table 2). Q is, however, considerably greater for the divalent than for the univalent cations.

Ion	$D_0 \cdot 10^5$ cm²/s	$s_{D.} \cdot 10^5$ cm²/s	Q cal/mole	s_Q cal/mole	$s_D \cdot 10^5$ cm²/s
Cd^{++}	72.3	8.2	9938	291	0.014
Ca^{++}	98.0	3.5	10693	878	0.039
Mg^{++}	183.1	8.3	13709	1033	0.003
Zn^{++}	101.0	2.7	12437	712	0.007
Pb^{++}	31.2	5.7	7277	1005	0.057

Table 2. The interdiffusion coefficients described by the relation $D = D_0 \exp(-Q/R\,T)$. s is the standard deviation.

Discussion

The Activation Energy

Q is decreasing both for the univalent and the divalent cations when the ionic radii increase, but Q for the divalent ions (Q^{++}) is considerably greater than the Q values for the univalent cations (Q^{+}), if ions with approximately the same radii are considered.

For our further discusison of Q we have made some assumptions about the sulphate lattice and the distribution of the cations in the lattice.

In the sulphate lattice there are three lattice positions available for two cations[3]. The two smallest of these, the tetrahedral positions, can only accomodate lithium ions and perhaps sodium ions, while the greater one has a free space of about 3.18 Å according to ØYE[4]. All the other studied cations must thus jump between the octahedral positions.

We have now assumed that the distribution of the cations is independent of the temperature and that the number of vacancies introduced by the addition of the divalent impurity cations can be neglected compared with the number of empty octahedral lattice positions.

Q can be written as the sum of a migration energy (Q_j) and a formation energy (Q_f). Q_f must here be considered as the energy to create a suitable empty octahedral position. Q_j is the energy which is needed for an ion to pass the potential barrier between two octahedral positions. Q_j for the univalent ion ($Q_j{}^{+}$) should then be half that of a divalent ion ($Q_j{}^{++}$), if ions with equal ionic radii are considered. On the other hand the formation energy should be independent both of the ionic radius and the valency.

We thus obtain

$$Q^{+} = Q_j{}^{+} + Q_f{}^{+}, \qquad Q^{++} = 2\,Q_j{}^{+} + Q_f{}^{+},$$

which gives

$$Q_j{}^{+} = Q^{++} - Q^{+}, \; Q_f{}^{+} = 2\,Q^{+} - Q^{++}. \qquad (1, 2)$$

Q_j and Q_f are both positive quantities and thus $2\,Q^{+} > Q^{++} > Q^{+}$. This agrees with our experimental results and we can now easily calculate Q_j and Q_f by comparing ions with approximately the same radii (Table 3).

Univalent cation	Divalent cation	Q_j kcal/mole	Q_f kcal/mole
Li	Zn, Mg	5.1	2.8
Na	Ca, Cd	4.2	3.0
K, Tl	Pb	1.5	2.9

Table 3. The migration energy and formation energy calculated from Eq. (1) and Eq. (2).

Q_j decreases when the cation radius increases, while the formation energy is constant and independent of the diffusing ion. This is in agreement with the model given above.

The Pre-Exponential Factor

No systematical investigations of D_0 for ionic compounds have been found in the literature. For metals D_0 generally falls between 0.1 and 0.5 with a comparably low accuracy.

As a general expression for D_0 one obtains

$$D_0 = g\,a^2\,\nu \exp\left((S_f + S_j)/R\right),$$

where g is a geometrical factor not far from unity, a a lattice parameter, ν the vibration frequency of the considered ion and S_f and S_j the entropies of formation and migration.

If we have the same transport mechanism for the different ions, g and a are independent of the diffusing ion. ν should be proportional to the inverse root of the reduced mass, but this relation can not ex-

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[3] A. KVIST, Thesis, Göteborg 1967.

[4] H. ØYE, Thesis, Trondheim 1963.

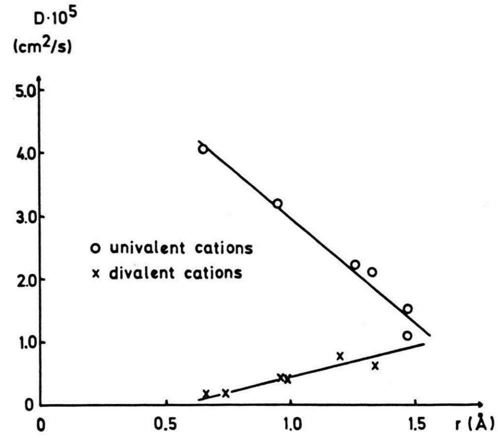

Fig. 2. The diffusion coefficients of univalent and divalent cations in cubic lithium sulphate as a function of the ionic radius at 700 °C.

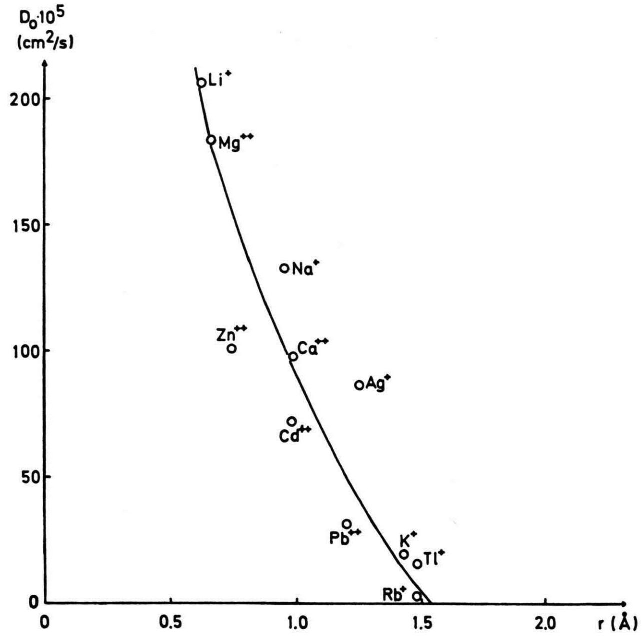

Fig. 3. The pre-exponential factor as a function of the ionic radius. →

plain the behaviour of D_0 when the ionic radius increases, see Fig. 3. The fast decrease in D_0 must thus be caused by a change in S_f or S_j.

From the Eqs. (1) and (2) we found that Q_f is independent of the diffusing ion and there are thus reasons to believe that also the formation entropy is constant for the different ions. On the other hand the decrease in Q_j should correspond to a simultaneous change in S_j.

It is seen in Fig. 3 that D_0 seems to go to zero (or to a very small value), when the ionic radius $r = 1.56$ Å, which should lead to very small diffusion coefficients for a greater ion. For the sulphate ion for instance (ionic radius 2.4 Å) the diffusion coefficient should thus be neglectable compared with the cations. It should also be observed that the value 1.56 Å is in good agreement with the radius of the octahedral position, 1.59 Å, found by ØYE[4] from X-ray investigations. The decrease in Q_j and S_j for the greater ions might thus be explained by a better fitting of these ions in the octahedral positions.

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