

The Isotope Effect of Electromigration in Some Solid Alkali Halides*

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The isotope effect of electromigration in some solid alkali halides was determined in their intrinsic ionic conductivity region. The external cationic mass effect (i. e., relative difference in cationic mobility/relative difference in mass) of lithium fluoride, chloride, bromide and iodide and potassium chloride was -0.243 , -0.207 , -0.195 , -0.190 and -0.254 , respectively, at 750, 540, 470, 370 and 600 °C, respectively. No difference of the mass effect was found between polycrystalline and single crystal potassium chloride. When the available data for the mass effect of the solid salts are plotted against the activation energy for electric conductance, there is a tendency for the mass effect to increase as the activation energy increases.

I. Introduction

To date, there have been very few measurements of the isotope effect of electromigration in solid salts, whereas many experiments have been carried out in molten salts¹. There have been, to our knowledge, five experiments on the isotope effect in solid salts published in the past: these are experiments on silver iodide², sodium chloride³, lithium sulfate^{4a, b}, lithium hydride⁵ and lithium fluoride⁶.

In regard to the isotope effect of self-diffusion in solid salts, there have been only three experiments on pure salts, viz. sodium chloride⁷, silver chloride⁸ and bromide⁸.

In order to elucidate the mechanism of atom movement in solid ionic salts, it is worthwhile to determine the isotope effect of electromigration in solid alkali halides, which can be regarded as the simplest and most typical ionic crystals. In the present work, the external cationic mass effect⁹ for lithium in its solid fluoride, chloride, bromide and iodide and for solid potassium chloride was measur-

ed and compared with the available data for other ionic crystals and molten salts.

Electromigration was carried out in the intrinsic ionic conductivity region. It has been estimated from conductivity data that the lithium halides are purely cationic conductors¹⁰. The cationic transport number of potassium chloride was re-examined, see below.

For the lithium salts, the isotope effect was only measured in polycrystals solidified from the molten state, while in the case of potassium chloride, both polycrystalline and single crystal material was studied.

II. Experimental

The electromigration cell used in the experiment with lithium chloride is shown in Fig. 1.

Sufficiently dried lithium chloride was melted in the U-shaped cell. After the salt was kept in the molten state for a few hours, it was slowly allowed to solidify. If any bubbles were found in the salt, it was remelted and allowed to solidify again. A few grams of potas-

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¹ Results are tabulated e. g. in books such as: A. KLEMM, Molten Salt Chemistry, ed. M. BLANDER, Interscience Publishers, New York, London 1964, p. 535, and A. KLEMM and K. HEINZINGER, Adv. Chem. Series **89**, 248 [1969].

² A. KLEMM, Naturwiss. **32**, 69 [1944]; Z. Naturforsch. **2 a**, 9 [1947].

³ M. CHEMLA and P. SÜE, C. R. Acad. Sci. Paris **236**, 2397 [1953]. — M. CHEMLA, Ann. Phys. **1**, 959 [1956].

⁴ a) A. LUNDÉN, Z. Naturforsch. **15 a**, 365 [1960]; J. Chim. Phys. **60**, 259 [1963]. — b) A. LUNDÉN, Z. Naturforsch. **17 a**, 142 [1962].

⁵ B. COLLÉN, Acta Chem. Scand. **18**, 839 [1964].

⁶ V. B. PTASHNIK and A. N. NAUMOV, Fiz. Trerdogo Tela (Soviet Phys. Solid State) **10**, 880 [1968].

⁷ L. W. BARR and A. D. LECLAIRE, Proc. Brit. Ceram. Soc. **1**, 109 [1964].

⁸ N. L. PETERSON and L. W. BARR, ANL-7155, p. 211 [1965].

⁹ The external cationic mass effect, μ_{ext} , is defined as: $\mu_{\text{ext}} = (\Delta u_{\text{iw}}/u_{\text{iw}})/(\Delta M/M)$, where $\Delta u_{\text{iw}}/u_{\text{iw}}$ is the relative difference in external cationic mobility, and $\Delta M/M$ the relative difference in mass¹. External mobilities are mobilities relative to the crystal lattice (in solids) or to the wall (in liquids). The internal mass effect refers to the mobilities of the cations relative to the anions. In this paper the mass effect is meant to be the external cationic mass effect, if not otherwise stated.

¹⁰ Y. HAVEN, Rec. Trav. Chim. **69**, 1471 [1950].



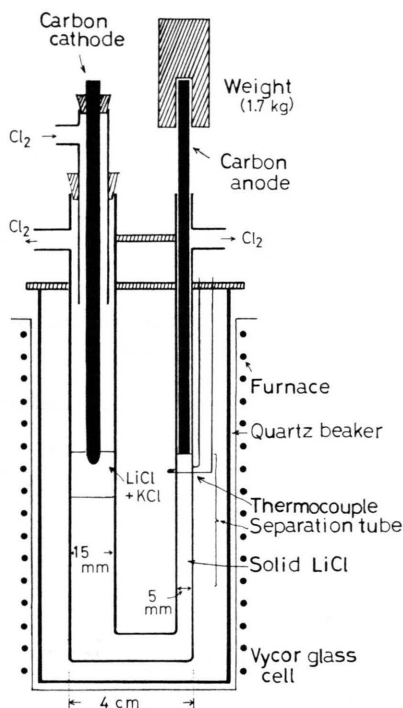


Fig. 1. Electromigration cell for LiCl.

sium chloride were added to the cathode compartment to give a molten mixture, which improved the contact between the cathode and the solid salt. On top of the carbon anode, a weight was placed, which pressed the anode against the salt that was gradually consumed during electromigration. Chlorine gas was introduced into the cathode compartment to convert as much electrodeposited metal as possible into the salt. The electric current was supplied through a constant current power supply circuit. During electromigration, the cathode was slightly corroded, and the salt near the cathode was contaminated, but the salt near the anode remained clean. The transported charge was measured with a copper coulometer.

After electromigration, the cell was cooled and sectioned into arbitrary lengths. For each section, the salt content was determined by titrating an aliquot of the lithium chloride solution with a silver nitrate solution. At the same time, the isotope ratio of the lithium was determined with an Atlas CH-4 mass spectrometer.

With lithium bromide, similar experiments were carried out.

In the case of lithium iodide, molten tin was employed as the cathode. The molten tin placed on top of the salt protected the salt from decomposing in contact with air and formed an alloy with the electrodeposited lithium metal.

In the case of lithium fluoride, an alumina cell was employed instead of a Vycor cell. The cell is shown in Fig. 2. In the alumina beaker containing molten lithium

fluoride, an alumina tube was inserted, and then the molten salt was allowed to solidify and electromigration was carried out. The quantity of lithium fluoride in each section was gravimetrically determined.

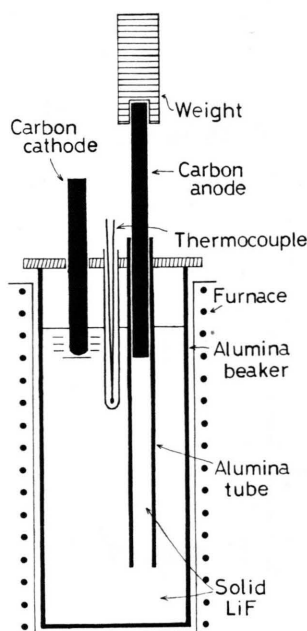


Fig. 2. Electromigration cell for LiF.

The experimental arrangement for potassium chloride is shown in Fig. 3. On a stainless steel plate we stacked a carbon anode, a slab of potassium chloride, one of barium chloride, a carbon cathode and another stainless steel plate. The whole stack was pressed together. The barium chloride served as an intermediate electrolyte to prevent decomposition of the potassium chloride. Dry argon gas was passed through the beaker in order to remove the chlorine gas that was generated at the anode and to protect the carbon from burning. The potassium chloride slab consisted either of a pellet, about 2 cm in diameter and 5 mm thick, made by pressing powder at 1000 kg/cm², or of a single crystal, about 1.5 × 1.5 × 0.5 cm³. The anode was a special carbon named "Toscoat carbon"¹¹, which was corroded very little by chlorine gas and did not contaminate the surface of the potassium chloride crystal. The transported charge was measured with a silver coulometer. After electromigration, the potassium chloride crystal was cooled and ground into sections from the anode side with emery paper. The potassium chloride powder from each section was weighed on a balance and, in order to check that no powder was lost in handling, the crystal was weighed before and after each sectioning. At the same time, the isotope ratio of potassium was determined for each section.

¹¹ It is a product made by Tokai-Denkyoku Co., Ltd. in Japan.

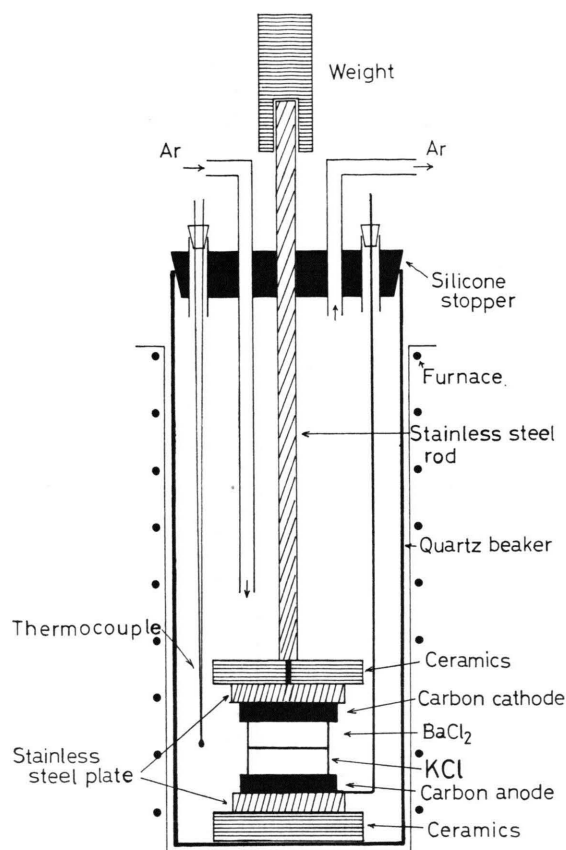


Fig. 3. Electromigration cell for KCl.

The transport number of potassium ions in potassium chloride at 600 °C was measured to be $^{12} 0.88 \pm 0.02$ with an apparatus which is similar to that used by TUBANDT and his coworkers^{13a}. This value is in agreement with some previous findings^{13a, b, c} although it does not agree with another one [0.71 ± 0.01 (600 °C)]¹⁴.

III. Results

The detailed results of one of the experiments are shown for lithium chloride and potassium chloride in Tables 1 and 6, respectively.

Table 1. Isotopic distribution after electromigration in LiCl (Exp. No. 1).

Fraction ^a No.	Quantity of LiCl (milliequiv.)	⁷ Li/ ⁶ Li
1	0.795	16.30 ± 0.02
2	0.919	16.31 ± 0.03
3	1.617	15.60 ± 0.02
4	1.867	14.89 ± 0.01
5	1.590	14.11 ± 0.03
6	4.244	13.83 ± 0.03
7	3.078	12.75 ± 0.02
8	3.282	12.15 ± 0.04
Before electromigration	—	12.24 ± 0.02

^a Fractions are numbered from the anode side.

Table 2. Mass effect in LiCl.

Experiment No.	1	2	3	4	5	6
Temperature (°C)	540 ± 10	540 ± 10	540 ± 10	540 ± 10	540 ± 10	540 ± 10
Electric current ^a (mA)	13	11	13	18	16	17
Duration (hr)	54	93	94	95	87	69
Transported charge (coulombs)	2549	3738	4413	6198	4940	4349
Diameter of separation tube (mm)	5.3	4.8	5.0	5.1	5.1	5.1
Current density (mA/cm ²)	61	60	66	92	78	89
Shift of anode						
Experimental (cm)	3.3	5.4	5.1	7.3	4.6	6.3
Calculated (cm)	2.5	4.4	4.8	6.7	5.1	4.7
Length of enrichment (cm)	1.53	2.27	2.26	1.47	1.53	1.28
Effective diffusion coefficient ^b (10^{-6} cm ² /sec)	3.8	4.9	4.8	2.0	2.4	2.1
Relative cationic mobility difference ^c	0.0315 ± 0.0012	0.0351 ± 0.0011	0.0338 ± 0.0009	0.0295 ± 0.0008	0.0277 ± 0.0009	0.0343 ± 0.0008
External cationic mass effect ^c	-0.205 ± 0.008	-0.228 ± 0.007	-0.220 ± 0.006	-0.192 ± 0.005	-0.180 ± 0.006	-0.223 ± 0.005

^a The applied voltage was between 250 and 300 V.

^b The effective (cationic) diffusion coefficients were estimated by the equation^{15a, b}: $D_{\text{eff}} = l^2 / \pi t$, where l is the length of enrichment, and t the duration of electromigration. The self-diffusion coefficient of LiCl has not yet been determined. The value estimated from the conductivity data¹⁰ by use of the Nernst-Einstein equation is about $4 \cdot 10^{-8}$ cm²/sec (540 °C). It is not explicable why D_{eff} is much higher than D_{self} .

^c The errors given are the standard deviations of the mean resulting from the errors in the chemical analysis, the mass spectrometric analysis and the readings of the coulometer.

¹² The error given is the standard deviation of the mean resulting from the errors in weighing the salt and reading the coulometer.

¹³ a) C. TUBANDT, H. REINHOLD, and G. LIEBOLD, Z. Anorg.

Allg. Chem. **197**, 225 [1934]. — b) C. WAGNER and P. HANTELMA, J. Chem. Phys. **18**, 72 [1950]. — c) G. RONGE and C. WAGNER, J. Chem. Phys. **18**, 74 [1950].

¹⁴ F. KERKHOFF, Z. Phys. **130**, 449 [1951].

Table 3. Mass effect in LiBr.

Experiment No.	1	2	3
Temperature (°C)	470 ± 10	470 ± 10	470 ± 10
Electric current (mA)	15	18	24
Duration (hr)	70	57.2	50.5
Transported charge (coulombs)	3662	3673	4266
Diameter of separation tube (mm)	5.1	5.3	5.1
Current density (mA/cm ²)	70	81	120
Shift of anode			
Experimental	6.1	5.6	7.7
Calculated	4.7	4.4	5.8
Length of enrichment (cm)			
Effective diffusion coefficient ^a (10 ⁻⁶ cm ² /sec)	7.8	5.4	1.9
Relative cationic mobility difference	0.0297 ± 0.0009	0.0305 ± 0.0006	0.0280 ± 0.0017
External cationic mass effect	-0.193 ± 0.006	-0.198 ± 0.004	-0.182 ± 0.011

^a $D_{\text{self}}(\text{LiBr}) \approx 5 \cdot 10^{-8}$ cm²/sec (470 °C) (from the conductivity data¹⁰). See the footnote ^b of Table 2.

From these data, the isotope effect has been calculated by a formula based on the material balance, which was originally presented by KLEMM¹⁵ and modified by the present authors¹⁶. The contamination near the cathode does not affect the calculation of the mass effect in the region near the anode.

The conditions and the results of all runs are summarized for lithium chloride, bromide, iodide and fluoride and potassium chloride in Tables 2, 3, 4, 5 and 7, respectively.

Table 5. Mass effect in LiF.

Experiment No.	1	2	3
Temperature (°C)	750 ± 10	750 ± 10	750 ± 10
Electric current (mA)	27	30	28
Duration (hr)	75	68	49
Transported charge (coulombs)	7353	7435	4942
Diameter of separation tube (mm)	6	6	6
Current density (mA/cm ²)	95	105	100
Relative cationic mobility difference	0.0385 ± 0.0012	0.0371 ± 0.0017	0.0355 ± 0.0017
External cationic mass effect	-0.250 ± 0.008	-0.241 ± 0.011	-0.231 ± 0.011

Table 6. Isotopic distribution after electromigration in KCl (Exp. No. 4). The enrichment length from the anode is calculated to be $8.0 \cdot 10^{-3}$ cm. From this value, the effective self-diffusion coefficient of K⁺ in KCl at 600 °C is roughly estimated to be $1.3 \cdot 10^{-10}$ cm²/sec. This value agrees well with that determined with a more accurate ordinary method ($D_{\text{K}^+} = 1.23 \cdot 10^{-10}$ cm²/sec at 600 °C)^b.

Fraction ^a No.	Quantity of KCl (milliequiv.)	³⁹ K/ ⁴¹ K
1	0.166	12.76 ± 0.02
2	0.141	13.12 ± 0.04
3	0.174	13.53 ± 0.02
4	0.228	13.84 ± 0.04
Before electromigration	—	13.88 ± 0.02

^a Fractions are numbered from the anode side.

^b J. F. LAURENT and J. BÉNARD, J. Phys. Chem. Solids **3**, 7 [1957].

Table 4. Mass effect in LiI.

Experiment No.	1	2	3	4
Temperature (°C)	370 ± 10	370 ± 10	370 ± 10	370 ± 10
Electric current (mA)	29	26	17	19
Duration (hr)	18	28	25	31
Transported charge (coulombs)	1888	2650	1523	2159
Diameter of separation tube (mm)	5	5	5	5
Current density (mA/cm ²)	150	130	90	95
Relative cationic mobility difference	0.0260 ± 0.0009	0.0257 ± 0.0011	0.0321 ± 0.0006	0.0283 ± 0.0011
External cationic mass effect	-0.169 ± 0.006	-0.167 ± 0.007	-0.209 ± 0.004	-0.184 ± 0.007

¹⁵ a) A. KLEMM, Z. Naturforsch. **1**, 252 [1946]. — b) A. KLEMM, Z. Phys. **123**, 10 [1944].

¹⁶ Relative difference in external mobilities of two (cationic) isotopes:

$$\Delta u/u = \frac{F(1+R_0)}{Q t_+ R_0} \left| \sum_i \frac{n_i(r_i - R_0)}{1+r_i} \right|.$$

R_0 : the isotope ratio before electromigration, r_i : the isotope ratio in the i -th fraction after electromigration, n_i : the equivalents of cations of interest in the i -th fraction, Q : the transported charge, t_+ : the cationic transport number. The summation is made from the fraction nearest to the anode to the fraction where no isotope enrichment is detected. See T. MORIMOTO, I. OKADA, and N. SAITO, to be published.

Table 7. Mass effect in KCl.

	Polycrystal		Single crystal	
Experiment No.	1	2	3	4
Temperature ($^{\circ}\text{C}$)	600 ± 10	600 ± 10	600 ± 10	600 ± 10
Electric current ^a (mA)	2.7	3.6	1.1	2.1
Duration (hr)	24	24	25	45
Transported charge (coulombs)	229	311	95	240
Cross section of crystal (mm)	ϕ 20	ϕ 20	15×15	15×15
Current density (mA/cm ²)	0.86	1.15	0.49	0.93
Relative cationic mobility difference ^b	0.0134	0.0123	0.0123	0.0128
	± 0.0015	± 0.0013	± 0.0013	± 0.0007
External cationic mass effect ^b	-0.268	-0.246	-0.246	-0.256
	± 0.030	± 0.026	± 0.024	± 0.014

^a The voltage was 300–500 V.

^b The errors correspond to the standard deviations of the mean for the quantitative determination of the salt, the readings of the coulometer, the mass spectrometric analysis and the transport number.

The external mass effects for lithium halides are calculated ¹⁷ on the assumption ^{6, 10} that the transport number of lithium is unity. If the transport number of lithium is actually less than unity, the external mass effect will increase in proportion to the decrease of the transport number.

IV. Discussion

Our result of the mass effect for lithium fluoride ($\mu_{\text{ext}} = -0.243 \pm 0.006$ at 750°C in polycrystal) is in good agreement with the previously determined one ($\mu_{\text{ext}} = -0.226, -0.241$ at 750°C in single crystal ⁷) within experimental error.

As can be seen from Table 7, the mass effects for polycrystalline material and the single crystals of potassium chloride agree with each other within experimental error.

These facts probably mean that, in the intrinsic temperature range, the contribution of grain boundary ionic conduction is low compared with that of bulk ionic conduction. They do not necessarily mean that the mechanism of electromigration is the same in both cases. At any rate, these facts suggest that the mass effects of polycrystals measured in the intrinsic temperature range will show those of the corresponding single crystals as well.

The results of the present investigation are summarized in Table 8 in order to compare them with related data obtained by other workers.

The mass effect of solid sodium chloride was reported to be -0.46 by CHEMLA and SÜE ³, which was, however, corrected to be between -0.22 and -0.29 by MANNING who re-analyzed their experimental data ¹⁸.

The duration of the experiment on lithium hydride ⁵ seems to have been too short to determine the mass effect accurately. Also, dendrites generated at the cathode spread even to the anode and gave rise to electronic conduction. As the author himself pointed out, the result for lithium hydride only provides a lower limit of the mass effect.

When the external mass effects of the solid salts studied by us are to be compared with those of the corresponding molten salts, the external mass effects of the molten salts, rather than the internal ones, should be taken into consideration. These can be estimated from the data for the internal mass effects and the transport numbers. Since the transport numbers have not yet been determined for molten lithium bromide and lithium iodide, the external mass effects for these melts cannot be calculated at present. For LiCl, the agreement between $\mu_{\text{ext}}(\text{solid})$ and $\mu_{\text{ext}}(\text{liquid})$ is good. In the case of potassium chloride, the difference is rather large, which indicates that the mechanisms of electromigration differ considerably.

The temperature dependence of the mass effect has not been determined in the present experiments. For lithium sulfate, no definite temperature depen-

¹⁷ Since in solid salts the external mass effects can be considered to have more physical significance than the internal mass effects, the former are calculated in the present work by use of the transport numbers. If the (cationic) transport

number is unity, the internal and external (cationic) mass effects have the same value.

¹⁸ J. R. MANNING, J. Appl. Phys. **33**, 2145 [1962].

Table 8. Cationic mass effects in solid and molten salts.

	Electromigration			Diffusion Solid salt $-(\Delta D/D)/(\Delta M/M)$
	Solid salt $-\mu_{\text{ext}}^a$	Molten salt $-\mu_{\text{int}}$	$-\mu_{\text{ext}}$	
KCl	0.254 ± 0.007 (600 °C)	0.074 (850 °C) ^b	0.12 ^c	—
NaCl	$0.22-0.29$ (750 °C) ^{3, 18}	—	—	0.368 ± 0.058 (614 °C) ⁷
LiF	0.243 ± 0.006 (750 °C)	—	—	—
	$0.21-0.24$ (600–750 °C) ⁶	—	—	—
LiCl	0.207 ± 0.008 (540 °C)	0.140 (720 °C) ^f	0.19 ^c	—
LiBr	0.195 ± 0.003 (470 °C)	0.148 (590 °C) ^g	—	—
LiI	0.190 ± 0.011 (370 °C)	0.15 (500 °C) ^g	—	—
Li ₂ SO ₄	0.14 (600–790 °C) ^{4a, b}	— (see ^h)	—	—
AgI	0.11 (230 °C) ²	—	—	—
LiH	> 0.04 (570 °C) ⁵	—	—	—

^a The errors given are the standard deviations of the mean of several measurements (electromigration).

^b S. JORDAN and A. KLEMM, Z. Naturforsch. **21a**, 1584 [1966].

^c See Refs. ^{d, e} for the transport numbers of potassium chloride and lithium chloride, respectively.

^d F. R. DUKE and A. L. BOWMAN, J. Electrochem. Soc. **106**, 626 [1959].

^e F. R. DUKE and A. FLEMMING, J. Electrochem. Soc. **106**, 130 [1959].

^f S. JORDAN, R. LENKE, and A. KLEMM, Z. Naturforsch. **23a**, 1563 [1968].

^g A. LUNDÉN, S. CHRISTOFFERSON, and A. LODDING, Z. Naturforsch. **13a**, 1034 [1958].

^h The internal mass effect of lithium has been measured to be -0.13 ± 0.02 in the eutectic mixture of Li₂SO₄–K₂SO₄ (80 mol-% Li₂SO₄: 625°–835 °C) ⁱ.

ⁱ A. LUNDÉN and V. LJUBIMOV, Z. Naturforsch. **23a**, 1558 [1968].

dence of the mass effect was detected over a wide temperature range ^{4b}, while for lithium fluoride, the mass effect increased slightly with rising temperature ^{6, 19}.

Incidentally, in the present experiments, the temperature was measured outside the crystal, and the effect of Joule heating can be disregarded because of the low current density.

With regard to the effect of impurities on the mass effect, it is unnecessary to seriously consider a very small amount of impurities in the intrinsic temperature range. In the present experiments, the purity was about 99.99 mol-% and 99.998 mol-% for the lithium salts and potassium chloride, respectively. For comparison, the mass effect for lithium chloride and potassium chloride respectively doped with 0.3 mol-% magnesium chloride and 0.4 mol-% strontium chloride is about 15% higher than that for the corresponding pure salts ²⁰.

When the available data on the mass effect for solid salts are plotted against the activation energy for electric conductance, there is a tendency for the mass effect to increase when the activation energy

increases, as shown in Fig. 4 *, **. In these salts almost all the charge is transported by the cations, and the activation energy for electric conductance is, therefore, equal to that for the cations.

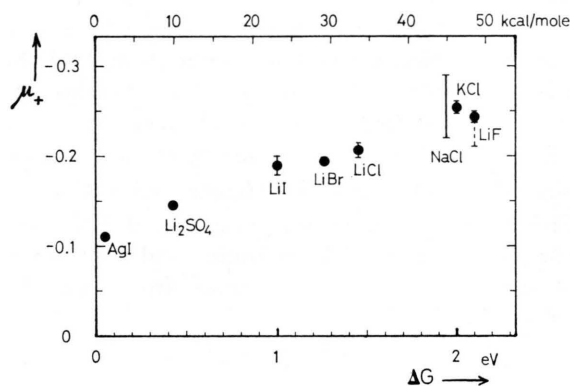


Fig. 4. Relationship between activation energy for electric conduction and external cationic mass effect in solid salts. For the activation energy data, see Ref. ³². The mass effect for LiF previously determined ⁶ is shown with a dotted line. Since quite divergent values have been reported for the activation energy for lithium hydride at 600 °C, that is, 0.53 eV * and 1.65 eV **, and only the lowest limit of the mass effect is known, the point for lithium hydride is omitted in the figure.

¹⁹ $-\mu_{\text{int}}(\text{LiF})$ ($= -\mu_{\text{ext}}$, assuming $t_+ = 1$) = 0.21 (600 °C), 0.24 (750 °C).

²⁰ T. MORIMOTO, unpublished.

* F. E. PRETZEL, G. N. RUPERT, C. L. MADER, E. K. STORMS, G. V. GRITTON, and C. C. RUSHING, J. Phys. Chem. Solids **16**, 10 [1960].

** A. BERGSTEIN and J. S. R. DIDIER, Czech. J. Phys. **18**, 538 [1968].

The isotope effect ε_e , that is, the relative external mobility difference, is related to the external mass effect μ_{ext} by

$$\varepsilon_e = (u_1 - u_2)/u = \mu_{\text{ext}}(M_1 - M_2)/M \quad (1)$$

where u is the external mobility, M the mass, and subscripts 1 and 2 indicate the lighter and heavier isotopes, respectively.

On the other hand, in the diffusion experiments, the isotope effect ε_d is usually expressed by ²¹

$$\varepsilon_d = (D_1 - D_2)/D = f \Delta K \{ (M_2/M_1)^{1/2} - 1 \} \quad (2)$$

(see Note ²²)

where D is the diffusion coefficient, f the Bardeen-Herring correlation factor and ΔK the fraction of the total translational kinetic energy which is possessed by a diffusing atom as it crosses the saddle point.

The transport mechanisms of electromigration and diffusion are not necessarily the same. In the former case, for example, only charged particles migrate, whereas in the latter, also neutral defect complexes, such as vacancy pairs diffuse. In fact, for sodium chloride, which is the only case for which the isotope effects in both electromigration ^{3, 18} and self-diffusion ⁷ have been determined experimentally, the mass effect of self-diffusion ²⁵ is considerably greater than that of electromigration, as shown in Table 8. It is impossible to know whether the difference exists or resulted from experimental errors. Anyway, according to MANNING's theory ²⁶, the correlation factor does not appreciably change under different driving forces. Thus, when we assume that the isotope effect of both electromigration and diffusion is the same, $-\mu_{\text{ext}}$ can be expressed from Eqs. (1) and (2) by

$$-\mu_{\text{ext}} = f \Delta K / 2. \quad (3)$$

²¹ For example, see J. G. MULLEN, Phys. Rev. **121**, 1649 [1961].

²² According to LECLAIRE ²³, Eq. (2) is not exact if ΔK is not equal to unity. For simplicity, Eq. (2) is adopted here. In the case of the collective diffusion of n atoms, ε_d is expressed by ^{8, 24}

$$\varepsilon_d = f \Delta K \left[\left\{ \frac{M_2 + (n-1)M}{M_1 + (n-1)M} \right\}^{1/2} - 1 \right]. \quad (2')$$

In that case, Eq. (3) would have to be changed into

$$-\mu_{\text{ext}} = f \Delta K / 2n. \quad (3')$$

²³ A. D. LECLAIRE, Phil. Mag. **14**, 1272 [1966].

²⁴ J. N. MUNDY, L. W. BARR, and F. A. SMITH, Phil. Mag. **14**, 785 [1966].

In the case of a vacancy mechanism, the Bardeen-Herring correlation factor is estimated to be 0.78 for a fcc lattice ²⁷. Even if this value is not exactly correct, the correlation factors seem to be nearly the same for the alkali halides listed in Table 8. Lithium sulfate also has a fcc lattice, and its so-called experimentally determined correlation factor ²⁸ decreases from about 0.9 to 0.7 as the temperature increases from 600° to 800 °C ²⁹. As the mass effect for lithium sulfate is independent of temperature, it follows from Eq. (3) that ΔK increases with temperature. As the correlation factor is almost identical in these alkali halides and lithium sulfate, the relative magnitude of the mass effect will depend mainly on that of ΔK .

On the other hand, silver iodide has a bcc lattice and the experimentally determined correlation factor is about 0.54, independent of temperature between 200° and 500 °C ²⁹. Its diffusion mechanism is complicated and not explicable by an interstitial-cy mechanism alone.

A possible correlation between ΔK and the activation volume has been suggested by BARR et al. ^{8, 24, 30}. In the case of self-diffusion in metals, for example, LE CLAIRE ²³ has roughly estimated that ΔK is correlated with the formation volume ΔV_f and the atomic volume ΔV_a :

$$\Delta K \sim 1 / \{ 1 + (n'/3) (1 - (\Delta V_f / \Delta V_a)) \} \quad (4)$$

where n' is approximately the number of atoms that relax during decay of the saddle point configuration. As for ionic salts, no quantitative relation between ΔK and ΔV_f has been suggested yet, but supposing that an equation similar to Eq. (4) holds, ΔK increases as $\Delta V_f / \Delta V_a$ increases.

On the other hand, according to KEYES ³¹, the activation volume ΔV is correlated with the activa-

²⁵ The entity in diffusion corresponding to the mass effect in electromigration, that is $(\Delta D/D)/(\Delta M/M)$, is named isotope factor, see A. LODDING, Adv. Chem. Series **89**, 264 [1969].

²⁶ J. R. MANNING, Phys. Rev. **139**, 126 [1965].

²⁷ K. COMPAAN and Y. HAVEN, Trans. Faraday Soc. **54**, 1498 [1958].

²⁸ R. J. FRIAUF, J. Appl. Phys. **33**, 494 [1962].

²⁹ A. KVIST and R. TÄRNEBERG, Z. Naturforsch. **25a**, 257 [1970].

³⁰ L. W. BARR and J. N. MUNDY, Diffusion in BCC Metals, American Society for Metals, Metals Park, Ohio 1965, p. 171.

³¹ R. W. KEYES, J. Chem. Phys. **29**, 476 [1958]; **32**, 1066 [1960].

tion energy for diffusion ΔG and the isothermal compressibility β as follows:

$$\Delta V = k \beta \Delta G \quad (5)$$

where k is a constant, and the activation volume for movement (ΔV_m) and the activation volume for formation (ΔV_f) are expressed respectively by

$$\Delta V_m = k \beta \Delta G_m, \quad \Delta V_f = k \beta \Delta G_f \quad (5')$$

where ΔG_m and ΔG_f are the activation energies³² for movement and formation, respectively. In the intrinsic temperature region in pure crystals of the Schottky type such as alkali halides,

$$\Delta V = \Delta V_f/2 + \Delta V_m.$$

Thus, ΔK is estimated to be associated with the activation energy for diffusion and, consequently, with that for electric conduction in the alkali halides

under discussion. However, for the moment we cannot quantitatively explain the relationship between ΔK and the activation energy for electric conduction since experimental data for β at high temperatures have not yet been obtained.

At any rate, it is not surprising that the mass effect increases for these alkali halides as the activation energy increases. In the case of lithium sulfate, a similar discussion would hold as for the alkali halides. It might be fortuitous that the mass effect for silver iodide falls in line with the alkali halides.

Experiments on potassium bromide, rubidium chloride, and potassium sulfate are now in progress, the results of which will make clearer the relationship between the mass effect and the activation energy.

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³² The activation energy for electric conductance is tabulated in: LANDOLT-BÖRNSTEIN, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik, 6th ed., Springer-Verlag, Berlin 1959, Band II, p. 223; R. J. FRIAUF, American Institute of Physics Handbook, McGraw-Hill, New York 1963, 2nd ed., p. 9–63.