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IONIC CONDUCTIVITY OF SOLID MIXTURES

by William L. Fielder Lewis Research Center Cleveland, Ohio



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Lewis Research Center Cleveland, Ohio

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SUMMARY

The conductivities of four solid mixtures were determined as a function of temperature: (1) the lithium fluoride - lithium chloride eutectic, (2) the lithium chloride potassium chloride eutectic, (3) the lithium fluoride - sodium chloride eutectic, and (4) a 50-mole-percent mixture of sodium chloride and potassium chloride. Two conductivity regions were obtained for each of the four mixtures. The activation energies for the conductivity for the lower-temperature regions ranged from 14 to 27 kilocalories per mole (59 to 114 kJ/mole). These energies were similar to the cation migration energies for the single crystals of the alkali halides. The conductivity of the mixtures in the lower-temperature regions is best explained by the following mechanism: (1) formation of cation vacancies primarily by multivalent impurities, and (2) migration of the cations through these vacancies.

The activation energies for the conductivity of the solid mixtures in the uppertemperature regions ranged from 5 to 9 kilocalories per mole (20 to 39 kJ/mole). These values are significantly smaller than those energy values that might be expected for a normal intrinsic process. The low activation energies may reflect an ion transport process through a liquid-like state (premelting) or along low-energy paths such as line or plane imperfections. Additional evidence is needed before a upper-temperature region mechanism can be suggested with certainty.

INTRODUCTION

The electrical conductivity of several ionic salts, both in the solid and liquid state, have been investigated as a function of temperature (refs. 1 and 2). The conductivity of ionic salt mixtures, however, has not been reported, except for a few cases (ref. 3).

In the present investigation, the ionic conductivities of four solid mixtures were measured, particularly at temperatures approaching the melting point. The four solid mixtures were (1) the lithium fluoride - lithium chloride (LiF-LiCl) eutectic, (2) the lithium chloride - potassium chloride (LiCl-KCl) eutectic, (3) the lithium fluoride sodium chloride (LiF-NaCl) eutectic, and (4) a 50-mole-percent mixture of sodium chloride (NaCl) and potassium chloride (KCl). The activation energies and the frequency factors, obtained from the electrical conductivity data for these solid mixtures, were compared with data available for the alkali halide salts and their mixtures in both the solid and liquid states. From this comparison, inferences were made of the probable conduction process.

EXPERIMENTAL

Preparation of Samples

Lithium fluoride - lithium chloride eutectic. - This single cation eutectic mixture (30.5-mole-percent LiF) melts at 501[°] C (ref. 4). Lithium chloride (99.9 percent with a loss on drying of 0.1 percent) was mixed in the proper ratio with LiF (99.9 percent) and placed in a 15-millimeter outside diameter quartz tube. This tube was placed in a larger quartz tube. All manipulations of the salts and mixtures were carried out in a dry box which was continually purged with gaseous nitrogen obtained as boil-off from liquid nitrogen. The mixture of the two salts was dehydrated by evacuation at room temperature through liquid-nitrogen traps for 2 to 3 days. Occasionally, dry helium gas was added to help remove traces of moisture. The salt mixture was heated slowly (over an 8-hr period) at about 10^{-3} torr (0.1 N/m²) to about 50^o C below its melting point. Then, about 1 atmosphere $(10 \times 10^4 \text{ N/m}^2)$ of hydrogen chloride gas was added: and the mixture was heated until fused. Hydrogen chloride gas suppresses the hydrolysis of LiCl which might result from any residual traces of water. Dissolved hydrogen chloride was removed from the melt by several evacuations and flushes with dry helium. Finally, the fused mixture was heated at a temperature of about 50° C above its melting point (at about 10^{-3} torr (0.1) N/m^2) for 20 to 30 minutes. The melt was shaken occasionally to help remove trapped bubbles of helium. The melt was cooled slowly with the bottom tip of the quartz tube slightly cooler than the bulk of the melt to initiate solidification at this tip. After cooling to about 100⁰ C below the melting point of the eutectic, the tube was filled with helium. On cooling to room temperature, the solid rod was removed from the tube in a dry box.

A small section (about 1 cm in length) was taken from the solid rod about one-third of the way from the bottom. This served as the polycrystalline sample of the eutectic of LiF-LiCl. The outer surfaces and faces of the sample were ground and polished with fine emery paper. The length and the outer diameter of the sample were measured with a micrometer.

Lithium chloride - potassium chloride eutectic. - This eutectic mixture of the composition of 41.4-mole-percent KCl (ref. 5) melts at 354.3° C (ref. 6). Anhydrous lithium chloride (99.9 percent) was mixed with KCl (99.9 percent with a loss on drying of 0.02 percent) in the proper ratio. Two solid samples were obtained in a manner similar to that used to obtain the LiF-LiCl eutectic. A sample of the LiCl-KCl mixture, containing a small quantity of calcium chloride was also prepared. The purified eutectic was crushed and mixed with anhydrous calcium chloride (99.7 percent purity) at a 0.12-mole-percent ratio. This mixture was dehydrated and heated to fusion in the manner described previously. Although the initial composition was about 0.12 mole percent, subsequent analyses (after conductivity measurements) indicated that this sample contained about 0.08-mole-percent calcium ions.

Lithium fluoride - sodium chloride eutectic. - This eutectic (41.5-mole-percent LiF) melts at 680° C (ref. 4). Two samples of this eutectic mixture were prepared using LiF (99.9 percent) and NaCl (about 99.5 percent) in the proper ratios.

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Sodium chloride - potassium chloride mixture. - While the three previous mixtures form eutectic systems, NaCl and KCl form a minimum melting mixture at about 50 mole percent. At this composition, KCl yields two crystalline phases up to about 470° C and a solid solution from about 470° C to the melting point of about 665° C (ref. 7). A sample of the 50-mole-percent mixture of NaCl and KCl was prepared in order to compare its conductivities with the three eutectic mixtures.

Analyses of the solid mixtures (after conductivity investigations) are shown in table I.

Conductivity Measurements

Two methods were used to produce electrical contacts on the crystal faces: sputtering with platinum in the absence of air and water vapor, and coating with several thin coats of an emulsion of colloidal graphite in dry benzene. Because the graphite method was easier and produced equally good contacts, colloidal graphite contacts were used on most of the samples.

Essentially, the same apparatus and procedure that had been used to determine the conductivities of the alkaline earth fluorides (refs. 8 and 9) were used in the study. A three-heat-zone furnace was used. Each zone was controlled by means of a saturable-core reactor in conjunction with a proportional control unit. The solid samples were heated and cooled slowly two or three times to within 25° to 50° C of the melting point in vacuum to remove benzene and traces of oxygen, water vapor, and other gaseous impurities. Helium gas, which had been purified by passage over fine copper turnings at about 375° C and through a liquid-nitrogen trap, was introduced into the system to a pressure of about 400 torr (5×10^4 N/m²). The temperatures of both electrodes were determined by means of calibrated platinum - platinum- 13-percent-rhodium thermocouples to a certainty of at least 0.2° C. The average of these two readings was taken as the temper-

ature of the solid sample.

The alternating-current (ac) method was used to measure resistances over the hightemperature region where resistances were less than 10^6 ohms. The ac measurements were made at 0.1 and 1 kilohertz with an impedance comparator bridge and standard resistors with an estimated accuracy of about 5 percent. For resistances greater than 10^6 ohms, the ac method does not give sufficiently accurate values. A direct-current (dc) method, using an electrometer, was employed for resistances above 10^6 ohms. All dc measurements were taken as rapidly as possible at low currents (10^{-4} to 1 mA) in order to prevent excessive electrolysis or polarization. Also, the polarity was reversed after each measurement to reduce these effects. The accuracy of the dc measurements is estimated to be about 10 percent.

RESULTS

The specific conductivities of the ionic solids were calculated from the resistance measurements as follows:

$$\kappa = \frac{l}{\rho a} \text{ ohm}^{-1} \text{ cm}^{-1} \tag{1}$$

where κ is the specific conductivity, ρ is the observed resistance (ohm), l and a are the length and area of the solid. For each ionic solid, the logarithm of the specific conductivity was plotted against the reciprocal of the absolute temperature (Arrhenius plot). The slopes, standard deviations, and the intercepts were determined by the method of least squares. Generally, two temperature regions with different slopes were obtained for each solid.

Lithium Fluoride - Lithium Chloride Eutectic

The data for the LiF-LiCl eutectic is shown in figure 1. The experimental activation energy, ΔE , and the frequency factor, A, were calculated from the Arrhenius equation:

$$\log \kappa = \log A - \frac{\Delta E}{2.303 \text{ RT}}$$
(2)

where R is the gas constant, and T is the absolute temperature. For the lower temperature region, about 16° to 70° C, an activation energy of 16.1±0.7 kilocalories per mole (67±3 kJ/mole) and a frequency factor of 2.0±0.5×10² per ohm per centimeter were

calculated. For the upper-temperature region, about 100° to 480° C, an activation energy of 6.5±0.1 kilocalories per mole (27.2±0.4 kJ/mole) and a frequency factor of about $1.7\pm0.2\times10^{-4}$ per ohm per centimeter were obtained. The parameters for both regions are listed in table II.

Lithium Chloride - Potassium Chloride Eutectic

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The specific conductivities of two samples of the eutectic of LiCl-KCl (A and B) are shown in the Arrhenius plot (fig. 2) for the temperature range of 108° to 345° C. These two samples gave essentially the same line (and slope) for this range. The activation energies (table II) for the two samples were in good agreement with the value obtained for the LiF-LiCl eutectic sample over its lower-temperature region. The conductivity of the LiCl-KCl eutectic doped with 0.08-mole-percent calcium chloride (solid C) is shown in figures 2 and 3. The lower-temperature region ranged from about 55° to 165° C. The activation energy for the doped sample (table II) for the lower region is quite similar to those values obtained for the undoped samples (A and B) suggesting that a similar mechanism is operating in this lower-temperature region for both the doped and undoped samples. An upper-temperature region was also obtained for the data (at 1 kHz) for the range of 295° to 352° C. The activation energy and frequency factor (table II) for this doped sample for the upper region was similar to those values listed previously for the LiF-LiCl sample.

Lithium Fluoride - Sodium Chloride Eutectic

The data for the two samples of the LiF-NaCl eutectic are shown in figure 4. The lower-temperature region ranged from about 175° to 440° C. The slope for the upper region decreases continuously as the melting point is approached. A straight line region (fig. 5) for the upper-temperature region was assumed for the range of about 520° to 665° C. The activation energies and the frequency factors for both temperature regions are given in table II.

Sodium Chloride - Potassium Chloride Mixture

The Arrhenius plot for the solid mixture of 50-mole-percent NaCl and KCl is shown in figure 6. A lower-temperature region was obtained between 185° and about 365° C

and an upper region between about 390° and 620° C. The activation energies and frequency factors are listed in table II.

DISCUSSION

Conduction in Solid Alkali Halides

Single crystals of an alkali halide (e.g., LiCl) conduct by means of ions rather than by electrons. The generally accepted mechanism (Schottky), for an intrinsic conduction in a real single crystal of an alkali halide, assumes that only point defects are involved. It also assumes that these point defects are formed by thermal movement or by impurities. For the first process, thermal movement of normal cations and anions, in equal numbers, from their lattice sites to the surface of the crystal produce cation vacancies and anion vacancies. Multivalent impurities may also produce point defects. For example, a divalent chloride in an alkali halide lattice will produce a cation vacancy in order to maintain electrical neutrality (ref. 1).

Both cations and anions of the alkali halide can migrate through the crystal by moving through the vacancies. Whether the migration of the cations or the anions will control the intrinsic conductivity will depend on the energy requirements of the respective species. In general, it is found that the cations are the primary conductors in alkali halides. For example, NaCl has a sodium ion transport number of 0.98 at 510° C and 0.93 at 625° C; and KCl has a potassium ion transport of 0.94 at 500° C and 0.88 at 600° C (ref. 1).

If only cations are migrating throughout the crystal, the specific conductivity of an alkali halide is proportional to the total number of the cation vacancies and to their mobilities (ref. 1). Both terms are exponential functions of the temperature. The specific conductivity for an alkaline halide can be expressed as follows:

$$\kappa = C \left[N_{I} + N_{O} \exp\left(\frac{\Delta S_{F}}{2R}\right) \exp\left(-\frac{\Delta H_{F}}{2RT}\right) \right] \left[\mu_{O} \exp\left(\frac{\Delta S_{M}}{R}\right) \exp\left(-\frac{\Delta H_{M}}{RT}\right) \right]$$
(3)

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where N_I is the number of defects per cubic centimeter produced by multivalent impurities, ΔH_F and ΔS_F are heat and entropy of formation of defects, ΔH_M and ΔS_M are the heat and entropy of migration of cation vacancies, T is the absolute temperature, and C, N_O , and μ_O are constants. For an intrinsic conductivity, it is assumed that the number of defects that are formed thermally is much greater than the number that are produced by impurities (i.e., N_I is negligible) and that the entropies of formation and migration are constants. The specific conductivity for the intrinsic region, therefore, simplifies to

$$\kappa_{\mathbf{I}} = \mathbf{A}_{\mathbf{I}} \exp\left(-\frac{\Delta \mathbf{H}_{\mathbf{I}}}{\mathbf{RT}}\right)$$
(4)

where A_I is the frequency factor and ΔH_I is the heat of activation for the intrinsic region.

An extrinsic region is often observed for solids at the lower temperatures. In this region, the number of defects that are formed by impurities is greater than that number that are formed thermally. Then, the total number of defects is essentially equal to N_{T} . If the entropy of migration is assumed to be constant, equation (3) reduces to

$$\kappa_{\rm E} = A_{\rm E} \, \exp\left(-\frac{\Delta H_{\rm M}}{\rm RT}\right) \tag{5}$$

where A_E is the frequency factor for the extrinsic region. For small-volume changes of the solid, the heat of activation ΔH can be replaced by the experimental activation energy ΔE . Introducing this change in equations (4) and (5) yields the following expressions for the specific conductivity for the intrinsic and extrinsic regions, respectively:

$$\kappa_{\mathbf{I}} = \mathbf{A}_{\mathbf{I}} \exp\left(-\frac{\Delta \mathbf{E}_{\mathbf{I}}}{\mathbf{RT}}\right) \tag{6}$$

$$\kappa_{\rm E} = A_{\rm E} \, \exp\left(-\frac{\Delta E_{\rm E}}{\rm RT}\right) \tag{7}$$

The activation energies for pertinent solid alkali halides (refs. 10 to 13) are given in table III for both the intrinsic and extrinsic regions. For the extrinsic region the cation migration energies ($\Delta H_M = \Delta E_E$) range from about 10 to 20 kilocalories per mole (42 to 83 kJ/mole). The preexponential factor A_E for the extrinsic region depends on the number of defects produced by the multivalent impurities N_I . Therefore, those values for A_E (given in table III) for the extrinsic region are specifically for the impurity levels listed.

Conduction in Fused Alkali Halides

Although a Schottky mechanism is widely accepted for conduction in solid alkali halides, there is no generally accepted mechanism for conduction in the fused state. Nevertheless, it has been suggested by Bloom that, if no constitutional changes occur

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in the liquid with changes in temperature, the specific conductivities can be expressed as follows (ref. 14):

$$\kappa = A_{C} \exp\left(-\frac{\Delta E_{C}}{RT}\right) + A_{A} \exp\left(-\frac{\Delta E_{A}}{RT}\right)$$
(8)

where ΔE_C and ΔE_A are the empirical energies of activation for the cation and anion, respectively, and the A_C and A_A are the respective frequency factors. If the two activation energies are nearly equal or very different, equation (8) simplifies to

$$\kappa = A_{L} \exp\left(-\frac{\Delta E_{L}}{RT}\right)$$
(9)

where $\Delta E_{T_{1}}$ is the observed activation energy.

Conductivities of three pertinent fused alkali chlorides (ref. 15), LiF (ref. 16), and the mixtures KCl-LiCl and NaCl-KCl (ref. 15) have been reported. In the present work, the experimental activation energies and frequency factors for the fused alkali chlorides were determined from the Arrhenius plots. These are summarized in table IV. The energies of activation for these fused halides are in the range of values associated with diffusional processes in the liquid state.

Conduction in Solid Mixtures of Alkali Halides

Lower-temperature region. - The observed activation energies of the solid mixtures for the lower temperature regions (table II) are not comparable to activation energies for intrinsic conduction of the constituent salts (table III) but are generally similar to activation energies for extrinsic conduction of the constituent salts. In all cases, however, the activation energy for the solid mixture was greater than that calculated for the simple additive effect of the constituent salts using the mole fraction as the weighing factor. This result is not unexpected because structural and impurity factors were not taken into account. At present, the effect of these factors on the conductivity of solid mixtures is not known.

Based on the activation energy values found for the four solid mixtures for the lowertemperature regions, it is reasonable to suggest that the conductivity of each mixture involves a process associated with extrinsic conductivity. The relations for extrinsic conductivity, derived from vacancy formation and ion migration consideration, are given in equations (5) and (7). These equations relate specific conductivity to ion-migration energy and experimental activation energy. Although the migrating ions were not identified in this study, it is of interest to speculate in this regard and also to compare the observed activation energies of the mixtures with the activation energy of the predominant migrating species in the constituent salts.

The LiF-LiCl eutectic is perhaps the simplest to treat, in that lithium ions are known to be the predominant migrating species in either LiF or LiCl which contain multivalent impurities (ref. 10). Therefore, it is plausible to suggest that the activation energy for the eutectic mixture represents the effective migration energy of lithium ions in this mixture. In considering the NaCl-KCl mixture, it is known that the migration energies of potassium and sodium ions (17 and 20 kJ/mole) in their respective chlorides are fairly close. Therefore, it seems reasonable to assume that both cations will contribute significantly to the conductivity for the 50-mole-percent mixture of NaCl and KCl. Consequently, the observed activation energy for the lower-temperature region should represent the effective migration energy of both cations in this mixture. It is more difficult to speculate concerning the eutectics of LiCl-KCl and LiF-NaCl. The smaller size of the lithium ions, relative to the sodium or potassium ions, would seem to favor the choice of the lithium ion as the predominant migrating species for either eutectic of LiCl-KCl or LiF-NaCl. In addition, the migration energy of the lithium ions, compared with the potassium or sodium ions in their respective halides, would seem to favor the lithium ion. On the other hand, the increased charge density of the lithium ion might tend to favor a decreased migration of the lithium ion.

Upper-temperature region. - As the temperature is increased, for the singlecrystal alkali halides, the number of defects which are produced by thermal agitation become greater than the number produced by impurities. At this point, the conductivity is said to change from extrinsic to intrinsic. Associated with the intrinsic conductivity are larger values of activation energy and frequency factor than observed in the extrinsic region. Such was not the case for the solid mixtures studied in this investigation. The activation energies and frequency factors for the solid mixtures decreased in the uppertemperature region by a factor of 1/2 to 1/3 of the lower-temperature values. This behavior suggests that the upper-temperature region conductivity process is quite different from the intrinsic conductivity process described earlier.

The activation energies obtained for the solid mixtures in the upper-temperature region are similar to energy values reported for fused alkali halides and for fused mixtures. Quite possibly, the low activation energies observed may reflect an ion-transport process through a liquid-like state (premelting). Alternately, the low values of activation energy may be a consequence of ion transport along low energy paths such as line and plane imperfections. For example, the energy of migration of silver ions in a deformed single crystal of silver bromide was 5.8 kilocalories per mole (24 kJ/mole) compared with 10 kilocalories per mole (42 kJ/mole) in an annealed single crystal (ref. 17). Nevertheless, at present, no inference as to the mechanism of conduction in

the upper-temperature region can be made.

As was mentioned previously, the solid mixture of 50-mole-percent NaCl-KCl is different from the other three mixtures in that a single phase is present over part of the upper-temperature region. The phase diagram indicates that the system changes from a two-phase solid to a solid solution at about 470° C. It is interesting to note that, in spite of a phase change, the activation energy is essentially constant, within experimental error, over this region (fig. 6).

SUMMARY OF RESULTS

The conductivities of four solid mixtures were determined as a function of temperature: (1) the lithium fluoride - lithium chloride eutectic, (2) the lithium chloride - potassium chloride eutectic, (3) the lithium fluoride - sodium chloride eutectic, and (4) a 50mole-percent mixture of sodium chloride and potassium chloride. Two conductivity regions were obtained for each of these four mixtures. The activation energies (14 to 27 kcal/mole (59 to 114 kJ/mole))for the conductivity for the lower-temperature regions were similar to those values reported for the cation migration energies for the constituent salts. It is suggested, therefore, that the conductivity of each mixture involves a process associated with extrinsic conductivity. The activation energies for the solid mixtures in the upper-temperature region decreased by a factor of 1/2 to 1/3 of the lower-temperature values. This is completely contrary to the behavior of the constituent salts and thereby indicates that the upper-temperature region conductivity process is not an intrinsic conduction process. The low-activation energies found may be a consequence of an ion-transport process through either a liquid-like state (premelting) or along lowenergy paths such as line and plane imperfections.

Lewis Research Center,

National Aeronautics and Space Administration, Cleveland, Ohio, March 13, 1968, 120-34-02-02-22.

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| LiF-LiCl eutectic | LiCl-KCl eutectic (solid A) | LiF-NaCl eutectic (solid A) | 50-Mole- percent NaCl and KCl | | |
|----------------------|--|--|--|--|--|
| Composition, wt. % | | | | | |
| Major | Major | Major | 0.01 to 0.1 | | |
| 0.1 to 1 | 0.1 to 1 | Major | Major | | |
| <0.01 | Major | 0.005 to 0.05 | Major | | |
| 0.005 to 0.05 | <0.01 | .005 to 0.05 | <0.01 | | |
| .005 to 0.05 | <. 01 | .005 to 0.05 | <. 01 | | |
| .005 to 0.05 | ^a N.D. | <0.01 | N.D. | | |
| <0.01 | N. D. | 0.005 to 0.05 | <0.01 | | |
| <. 01 | N.D. | <0.01 | N.D. | | |
| <. 01 | <0.01 | <. 01 | <0.01 | | |
| <. 01 | N.D. | <. 01 | N.D. | | |
| | LiF-LiCl eutectic Major 0.1 to 1 <0.01 0.005 to 0.05 .005 to 0.05 .005 to 0.05 <0.01 <.01 <.01 <.01 | $\begin{array}{c c} {\rm LiF-LiCl} \\ {\rm eutectic} \\ \end{array} \begin{array}{c} {\rm LiCl-KCl} \\ {\rm eutectic} \\ ({\rm solid} \ A) \\ \hline \\ \\ {\rm Compos} \\ \hline \\ {\rm Major} \\ 0.1 \ to \ 1 \\ < 0.01 \\ 0.1 \ to \ 1 \\ < 0.01 \\ 0.1 \ to \ 1 \\ < 0.01 \\ 0.005 \ to \ 0.05 \\ < 0.01 \\ 0.05 \ to \ 0.05 \\ < 0.01 \\ {\rm N.D.} \\ < .01 \\ < .01 \\ < .01 \\ {\rm N.D.} \\ \end{array}$ | $\begin{array}{c c c} {\rm LiF-LiCl} \\ {\rm eutectic} \\ {\rm eutectic} \\ {\rm eutectic} \\ {\rm (solid \ A)} \\ \end{array} \begin{array}{c} {\rm LiF-NaCl} \\ {\rm eutectic} \\ {\rm (solid \ A)} \\ \end{array} \begin{array}{c} {\rm LiF-NaCl} \\ {\rm eutectic} \\ {\rm (solid \ A)} \\ \end{array} \\ \hline \\ {\rm Composition, \ wt. \ \%} \\ \end{array} \\ \begin{array}{c} {\rm Major} \\ {\rm 0.1 \ to \ 1} \\ {\rm <0.01} \\ {\rm <0.01} \\ {\rm <0.05 \ to \ 0.05} \\ {\rm <0.01} \\ {\rm <0.05 \ to \ 0.05} \\ {\rm <0.01} \\ {\rm <0.05 \ to \ 0.05} \\ {\rm <0.01} \\ {\rm <0.05 \ to \ 0.05} \\ {\rm <0.01} \\ {\rm <0.05 \ to \ 0.05} \\ {\rm <0.01} \\ {\rm <0.05 \ to \ 0.05} \\ {\rm <0.01} \\ \end{array} $ | | |

TABLE I. - SPECTROGRAPHIC ANALYSIS OF SOLID MIXTURES

 $^a{}_{N\cdot\,D\cdot}$ - not detected.

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TABLE II. - ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR SOLID MIXTURES

| Composition, | Lower-te | emperature r | egion | Upper-temperature region | | | |
|---|-------------------------------|--|-----------------|--------------------------------|--|----------------|--|
| mole percent | Frequency factor, | Experimental activation energy, ΔE | | Frequency factor, | Experimental activation energy, ΔE | | |
| | $(ohm^{-1})(cm^{-1})$ | kcal/mole | kJ/mole | $(ohm^{-1})(cm^{-1})$ | kcal/mole | kJ/mole | |
| 30.5 LiF-69.5 LiCl | 2.0 \pm 0.5×10 ² | 16.1 ± 0.7 | 68±3 | $1.7\pm0.2{\times}10^{-4}$ | 6.5 ± 0.1 | 27.2 ± 0.4 | |
| 58.6 LiCl-41.4 KCl | 1.6 ± 0.2 | 15.6±0.2 | 65.4±0.8 | | | | |
| | 1.2 ± 0.1 | $15.2{\pm}0.2$ | 63.6±0.8 | | | | |
| 58.6 LiCl-41.4 KCl doped with 0.08 CaCl ₂ | ~. 9 | 14.0±0.2 | 58.6±0.8 | ~1×10 ⁻⁴ | ≈5 | ≈21 | |
| 41.5 LiF-58.5 NaCl | $.6\pm0.1$ | 20.4±0.6 | 86±3 77, 5+1 | ~1×10 ⁻⁴ | ≈8 | ≈33 | |
| 50.0 NaCl-50.0 KCl | 2.6 \pm 0.4×10 ² | 27.3 ± 0.4 | 114 ± 2 | 2.3 \pm 0.5×10 ⁻⁴ | 9.4±0.8 | 39±3 | |

| Solid | Intrinsic region | | | Refer- | Extrinsic region | | | | Refer- |
|-------|---|-------------|--------------|--------|---|-----------------------------------|---------|------------------------|--------|
| | Frequency | Experimenta | l activation | ence | Frequency | Frequency Experimental activation | | Impurity, | ence |
| | A, (ohm ⁻¹)(cm ⁻¹) | kcal/mole | kJ/mole | | A, (ohm ⁻¹)(cm ⁻¹) | kcal/mole | kJ/mole | more percent | |
| LiF | 3.0×10 ⁶ | 45.8 | 192 | 10 | 0.4 | 15 | 63 | <0.06 MgF ₂ | 10 |
| LiC1 | 2.51×10 ⁶ | 33.8 | 142 | 10 | . 6 | 9.4 | 39 | .036 MgCl ₂ | 10 |
| NaCl | 5×10 ⁵ | 42.3 | 177 | 11 | . 8 | 19.5 | 82 | ~.01 Ca ions | 12 |
| ксі | 2.1×10 ⁵ | 43.7 | 183 | 13 | .7 | 17 | 72 | .05 SrCl ₂ | 13 |

TABLE III. - ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR SOLID ALKALI HALIDES

TABLE IV. - ACTIVATION ENERGIES FOR FUSED

HALIDES AND THEIR MIXTURES

[Estimated from data of refs. 15 and 16.]

| Composition, | Frequency | Observed activation | | |
|--------------------|-------------------------------|---------------------|---------|--|
| mole percent | factor, | energy, ΔE | | |
| | $^{A,}_{(ohm^{-1})(cm^{-1})}$ | kcal/mole | kJ/mole | |
| LiF | 20 | 2.2 | 9.2 | |
| LiCl | 13 | 1.5 | 6.3 | |
| NaCl | 9 | 1.9 | 8.0 | |
| KCI | 7 | 2.3 | 9.6 | |
| 41.2 KCl-58.8 LiCl | 18 | 3.4 | 14 | |
| 48.8 NaCl-51.2 KCl | 8 | 2.2 | 9.2 | |

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Figure 1. - Specific conductivity of lithium fluoride - lithium chloride eutectic solid.





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Figure 3. - Specific conductivity of lithium chloride - potassium chloride eutectic solid C; doped with 0. 08-mole-percent calcium chloride.



Figure 4. - Specific conductivity of lithium chloride - sodium chloride eutectic solid.





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Figure 5. - Specific conductivity of lithium fluoride - sodium chloride eutectic solid A; ac measurement method.



Figure 6. - Specific conductivity of 50-mole-percent sodium chloride - potassium chloride mixture; dc measurement method.

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