The upper flocculation zone corresponds to the flocculation of a positive sol, the lower to that of a negative sol. All those cases in which complete flocculation occurred when 2 cc. of electrolyte was added to 2 cc. of sol and allowed to stand for four hours are listed as the "Complete" flocculation zone under the column headed "Flocculation." All other cases in which complete flocculation occurred or which showed turbidity at the end of seventy-two hours are placed in the "Partial" flocculation zone. "No flocculation" corresponds to the samples in which no turbidity was manifest at the end of seventy-two hours.

A comparison of the properties of this sol is being made with the properties of a sol that has been recharged with potassium ferrocyanide. The effect of H^+ ion concentration on an irregular series for colloidal ferric oxide is being studied using potassium ferrocyanide as the recharging agent.

Summary

1. Negative colloidal hydrous ferric oxide has been prepared by hydrolysis of a suspension of Prussian blue.
2. Some of the properties of the sol have been studied.

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[Contribution from the Department of Chemistry of the University of Illinois]

TEMPERATURE-CONDUCTANCE CURVES OF SOLID SALTS. III. HALIDES OF LITHIUM

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The temperature–conductance curves of the solid halides of sodium and potassium have been investigated[2,3] and found in most cases to exhibit two distinct slopes when plotted to the axes log k (logarithm of the specific conductance) against $1/T$ (reciprocal of the absolute temperature). It was suggested by one of the writers[2] that the change of slope is probably significant of a change in the mechanism of conduction. Pursuant of this suggestion, transference experiments were performed upon sodium chloride[4] which indicated that only the sodium ion takes part in the conduction process over the temperature range of the lower slope, while in the higher temperature range both ions contribute to the conduction.

With the assumption that the conductance of a solid is proportional to the number of ions in its lattice which have an energy greater than a

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[1] This paper is an abstract of a thesis submitted by D. C. Ginnings in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Phipps, Lansing and Cooke, This Journal, **48**, 112 (1926).

[3] Phipps and Partridge, *ibid.*, **51**, 1331 (1929).

[4] Phipps and Leslie, *ibid.*, **50**, 2412 (1928).

certain threshold value, it was shown[2] that the slope of the log k–$1/T$ curve may be interpreted as measuring the "heat of liberation" which the conducting ion or ions must acquire in order to participate in the conduction process. From this point of view the lower slope (*i. e.*, the slope found in the lower temperature range) for sodium chloride measures the "heat of liberation" of a sodium ion in the sodium chloride lattice and the upper slope is a measure of the combined "heats of liberation" of a sodium and a chloride ion.

It was the purpose of this investigation to determine whether the temperature–conductance data of solid lithium halides can be represented satisfactorily by the log k–$1/T$ relation, to compare the conduction process in the lithium halides with that in the sodium and potassium series, and finally to attempt a correlation of the heats of liberation found in the different series.

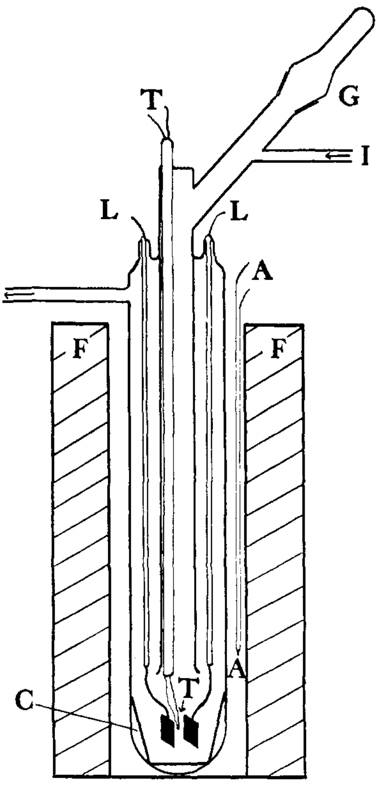


Fig. 1.—Conductivity apparatus.

Experimental

Method and Apparatus.—Because of the extreme hygroscopic character of the chloride, bromide and iodide of lithium, a new method was necessary. In previous work[2,3,4] a crystal or a high-pressure pellet had been clamped between two electrodes, and the conductance had been measured in a furnace open to the air. Two precautions were taken with the lithium halides. First, all water was removed and any lithium hydroxide formed by hydrolysis of the halide at high temperatures was converted back to the halide. This was accomplished by passing dry halogen acid gas over the molten salt for an extended period. Second, no moisture should be allowed to reach the salt. This was accomplished by carrying out all operations in an atmosphere of dry nitrogen.

The apparatus shown in Fig. 1 was constructed of pyrex glass and platinum. The salt was introduced through a ground-glass joint G into the platinum crucible C, which enclosed two platinum electrodes and a platinum–platinum-rhodium thermocouple T. The apparatus was placed in a furnace F, the temperature of which was controlled by a chromel–alumel thermocouple A in conjunction with an automatic temperature regulator made in this Laboratory. The appropriate dry halogen acid gas was passed in at I over the molten salt in the platinum crucible until all moisture had been removed and all hydroxide converted to the halide. The halogen acid gas was then swept out with dry nitrogen and the salt was allowed to cool and form a crystal or conglomerate of crystals around the electrodes and thermocouple.

The electrical conductivity of the salt was measured in much the same manner as in previous investigations.[2,3] An alternating current Wheatstone bridge was used at the higher temperatures for resistances up to one megohm. An alternating current of about 1200 cycles was supplied by a vacuum tube oscillator, and the bridge was designed to conform with suggestions of Jones and Josephs.[5] At lower temperatures, where resistances were greater than one megohm, a direct current deflection method was used. The source of e. m. f. for medium resistances was a potentiometer, and for high resistances, a high voltage "B" battery. The current was measured by a galvanometer having a sensitivity of about 5×10^{-11} amperes per mm. at a scale distance of three meters. To reduce polarization of the crystal the current was passed for only a few seconds at a time and was never allowed to exceed about 10^{-8} amperes.

A platinum–platinum-rhodium thermocouple was used with a Weston Universal potentiometer for measuring the temperature. The thermocouple was calibrated twice during the investigation against the boiling points of water, naphthalene, benzophenone and sulfur, and against the melting point of potassium chloride. A maximum deviation from the standard of about two degrees was observed at the highest temperatures.

Purification of Salts.—On account of the importance of purity of salts in conductance work, extreme care was taken in the preparation of the pure lithium halides. Suggestions by Richards and Willard[6] were followed. Mallinckrodt's "c. p." grade of lithium chloride was the basic material used. This was dissolved, treated with solid lithium carbonate and filtered, to remove a large part of the iron impurity. The chloride was converted to the nitrate and recrystallized several times to remove calcium, magnesium and iron. The nitrate was then converted to the carbonate, dissolved with carbon dioxide as the bicarbonate and reprecipitated as the carbonate by heating. This last reprecipitation was repeated to remove the remaining traces of alkali metal impurities. The pure halides were made by adding the appropriate halogen acid to the pure carbonate. The halogen acids were of c. p. grade, and were redistilled in pyrex, with the exception of hydrofluoric acid which was redistilled in platinum. Spectroscopic tests on the purified salts showed a very faint sodium line in contrast with the exceedingly strong line from the original material.

The melting points of the chloride, bromide and iodide were, respectively, 606, 551 and 467°. The values given in the "International Critical Tables" are, respectively, 613, 547 and 446°.

Experimental Results

General Discussion.—The data for one sample each of lithium chloride, lithium bromide and lithium iodide are plotted in Fig. 2. The slopes of the curves for two samples of each salt are averaged in Table I. It is apparent that there is a break in all the curves. Unlike the behavior observed previously for sodium and potassium halides, evidence appears here of two different lower slopes, one the result of a. c. and the other the result of d. c. measurements. In the case of lithium chloride and lithium bromide the d. c. lower slope differs from the a. c. lower slope by an amount considerably greater than can be ascribed to experimental error; in the case of lithium iodide the two lower slopes are the same. In the case of potassium halides, an anomalous behavior of the a. c. points in the region of transition from the upper to the lower slope has already been commented upon.[3] This so-called "a. c. anomaly" was evident in

[5] Jones and Josephs, This Journal, **50,** 1049 (1928).

[6] Richards and Willard, *ibid.*, **32,** 4 (1910).

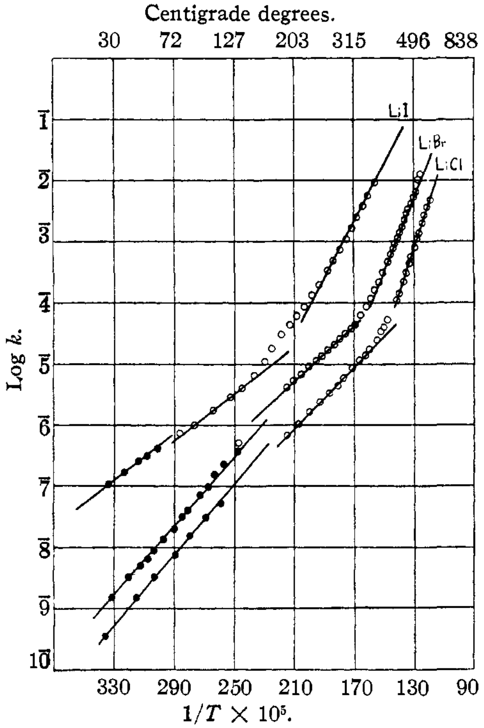
TABLE I

HEATS OF LIBERATION

	$E \times 10^{-3}$ cal. per g. mole (upper slope)	$e_1 \times 10^{-3}$ cal. per g. ion (lower slope)	$e_2 \times 10^{-3}$ cal. per g. ion $(E - e_1)$	T_m, melting point, °K.
LiCl	32.6	13.6	19.0	879[a]
LiBr	28.0	12.8	15.2	824[a]
LiI	21.2	8.4	12.8	740[a]
NaCl	39.8	20.2	19.6	1077
NaBr	38.4	18.4	20.0	1028
NaI	28.3	13.8	14.5	924
KCl	46.6	22.8	23.8	1043[a]
KBr	45.4	22.4	23.0	1006[a]
KI	37.2	19.6	17.6	952[a]

[a] Experimental values determined for the salts used in these investigations.

larger values of conductance by the a. c. than by the d. c. method in the transition region. The same general result is observable here in the lithium series, except that the a. c. values do not deviate as markedly from the extrapolated d. c. slope as was the case for the potassium halides. In the potassium series, there was little doubt that the a. c. anomaly arose from an inherent defect of the a. c. method in the transition region. Similarly in the lithium series it is probable that the a. c. lower slope is untrustworthy due to the same defect. Accordingly in Table I the a. c. lower slope is disregarded and the calculations of "heats of liberation" (e_1 values) are made from the d. c. lower slopes.



O, A.c.; ●, d.c.

Fig. 2.—Conductance of lithium chloride, lithium bromide and lithium iodide. Only one sample of each is graphed but data on two samples of each salt are averaged in Table I.

Heats of Liberation.—The applicability to salt conduction of the van't Hoff relation

$$\frac{\mathrm{d} \ln k}{\mathrm{d}T} = E/RT^2 \qquad (1)$$

has been discussed in a previous paper.[2] In this equation k is the specific conductance in mhos and E is a quantity of heat.

This expression may be written

$$E = -R\frac{\mathrm{d}\ln k}{\mathrm{d}(1/T)} \tag{2}$$

E may be interpreted as the "heat of liberation" of a gram-ion of the conducting ion species in a crystal lattice, and $\mathrm{d}\ln k/\mathrm{d}(1/T)$ is the slope of the conductance curve when plotted to the axes $\ln k$ against $1/T$. Equation 2 becomes

$$E = -4.58 \times \frac{\mathrm{d}\log k}{\mathrm{d}(1/T)} \tag{3}$$

where E is given in calories per gram ion.

Table I gives the heats of liberation calculated by Equation 3 from the lower and upper slopes of the three lithium halides. Values from two runs upon each halide were averaged in the table. For purposes of comparison the corresponding values for sodium and potassium halides are presented in the same table. Column 2 gives the values of $E \times 10^{-3}$ in calories per gram mole, as calculated from the upper slopes. Column 3 gives values of $e_1 \times 10^{-3}$ in calories per gram ion (alkali metal ion) as calculated from the d. c. lower slope. Column 4 gives values of $e_2 \times 10^{-3} = (E - e_1) \times 10^{-3}$. The e_2 values are interpreted as "heats of liberation" of the halide ions. Column 5 gives the melting points of the salts used in these investigations.

No data for lithium fluoride are found in this table. Due to its high melting point it was impossible to use the pyrex apparatus utilized for the other halides. Contrary to expectations, it was found to hydrolyze considerably when melted in air and to attack the platinum crucible. When dry hydrogen fluoride gas was passed through the melt the platinum crucible was no longer attacked. However, measurements of the conductance in air were not entirely satisfactory. It soon became apparent that a more refined technique will be necessary. Measurements in the neighborhood of the melting point indicated a very rapid increase in conductance at a temperature above 500°. This behavior is quite similar to that observed with sodium fluoride.[2] Change in crystal form in the neighborhood of the melting point is a possible explanation of this unusual behavior. An independent study of alkali fluorides will probably be undertaken in the future.

Discussion of Results

Table I reveals the following interesting generalizations. I. In a series of alkali halides having a common halogen, the lighter the alkali metal the less is the "heat of liberation" of either the alkali ion or the halide ion in the lattice. This is evident for example in the decreasing values of e_1 and e_2 in the series potassium chloride to lithium chloride.

II. In a series of alkali halides having a common alkali metal, the lighter the halide ion the greater the "heat of liberation" of either the halide ion or the alkali metal ion. This is evident for example in the increasing values of e_1 and e_2 as one goes from lithium iodide to lithium chloride. The exception to this rule in the e_2 value of sodium bromide may possibly be due to experimental error in the sodium series.

III. In the lithium series the relation $E = AT_m + B$ holds quite well. T_m is the melting point in degrees Kelvin and the constants A and B have the values, respectively, 83.6 and -40.8×10^{-3}. In the sodium and potassium series, perhaps due to experimental error in the earlier determinations of E, a linear equation is not adequate.

Summary

The temperature–conductance curves of solid lithium halides have been determined between room temperatures and temperatures near the melting point. Two slopes were found for the lithium halides, a behavior previously observed for the sodium and potassium halide series. This is taken to indicate a similarity in the conduction process in all three series. If this interpretation is correct, the lithium ion alone conducts at lower temperatures and both lithium and halide ions take part in the conduction at higher temperatures.

A comparison of the "heats of liberation" of the conducting ions in the different series, as calculated from the slopes of the conductance curves, has led to three generalizations. In the incomplete lithium series the "heat of liberation" appears to be a linear function of the temperature of the melting point.

URBANA, ILLINOIS

[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

THE JAMIN EFFECT IN CYLINDRICAL TUBES

BY W. O. SMITH[1] AND MILTON D. CRANE[2]

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About the middle of the last century Jamin[3] noticed that an ordinary cylindrical capillary tube filled with a chain of alternate air and water bubbles is capable of sustaining a finite pressure. If a series of constrictions is placed in the tube, the pressure sustenance is considerably increased. Each of these two effects, which might be termed the cylindrical and non-cylindrical, respectively, is referred to by Jamin's name. The writers have investigated the former, and conclude from their work that careful cleaning and avoidance of contamination render a cylindrical capillary incapable of sustaining pressure.

[1] Industrial Fellow, Mellon Institute of Industrial Research, Pittsburgh, Pa.

[2] This work was done while the junior author was a senior student in the School of Mines, University of Pittsburgh.

[3] M. J. Jamin, *Compt. rend.*, 50, 172–176, 311–314, 385–389 (1860).