The shift of the absorption band toward the violet end of the spectrum, which occurs with increasing dilution of sulfuric acid solutions of ferrous sulfate saturated with nitric oxide, also occurs on diluting phosphoric acid solutions of ferrous phosphate, and alcohol solutions of ferrous chloride saturated with nitric oxide. This shift of the absorption band indicates a transition of one compound into another. The transition of the three pairs of compounds having, respectively, the empirical formulas $FeSO_4 \cdot NO$, $FeHPO_4 \cdot NO$, $FeCl_2 \cdot NO$ is probably determined in each case by the activity of the water in the solutions, that is, the transition occurs when the aqueous tensions of the solutions reach the same numerical value. This condition obtains when the concentrations of the three solvents H_2SO_4, H_3PO_4 and C_2H_5OH are, respectively, about 65, 88 and 97%.

The function of the concentrated acids and alcohol is probably largely that of dehydrating the complex ion which exists in dilute solutions.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

TEMPERATURE–CONDUCTANCE CURVES OF SOLID SALTS.
II. HALIDES OF POTASSIUM AND THALLIUM

BY T. E. PHIPPS AND E. G. PARTRIDGE[1]

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In a recent investigation[2] of temperature–conductance curves of the solid halides of sodium, the data in most cases showed two distinct slopes when plotted to the axes log k (logarithm of specific conductance) against $1/T$ (reciprocal of the absolute temperature). In the discussion of these data it was assumed that the conductance of the solid is proportional only to the number of ions in its lattice which have an energy greater than a certain threshold value and, further, that the mobility of these ions is nearly independent of the temperature. With these assumptions it was shown that the slope of the log k–$1/T$ curve may measure the threshold energy (designated as heat of liberation) which the conducting ion or ions must acquire in order to participate in the conduction process. To explain the existence at higher temperatures of a second slope, which was within experimental error double the slope at lower temperatures it was assumed[3] that at higher temperatures both ions take part in the conduction

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[1] This paper is an abstract of a thesis submitted by E. G. Partridge 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] A subsequent investigation by Phipps and Leslie [*ibid.*, **50**, 2412 (1928)] of transference numbers in solid sodium chloride at high temperatures gives definite evidence that both ions conduct at high temperatures.

process. At low temperatures experimental evidence has already been adduced in the case of sodium chloride that only the sodium ion conducts.[4]

In continuing this work it seemed desirable first to test the adequacy of the log k–$1/T$ relation to represent experimental data for uni-univalent salts of widely different polarity, and thus to determine whether or not the concept of heat of liberation of the conducting ion is a fundamental one. Second, if heat of liberation appears to be a fundamental lattice property, it is of interest to discover its possible relation to other lattice quantities such as the natural quantum of the lattice, the lattice energy and the property vaguely designated as polarity.

We may state briefly the principal results of this investigation. The log k–$1/T$ relation is judged to be adequate to represent the conductance data of both potassium and thallous halides. The two-slope behavior found previously for sodium halides also characterizes the conductance curves of potassium halides. Thallous halides show a single slope only. The heat of liberation of the potassium ion decreases in the series chloride to iodide, as in the sodium series. The heat of liberation of the potassium ion is distinctly greater than that for the sodium ion in the corresponding halide. An approximately linear relation exists in the sodium and potassium series between heat of liberation and melting point.

Experimental

Apparatus.—The conductivity apparatus was similar to that used previously except that the base was made from a large nickel disk about 6.5 cm. in diameter and 3.0 cm. in thickness, recessed to a depth of 1.5 cm. The diameter of the recessed hole was about 3.6 cm. This large mass of nickel served to smooth out temperature fluctuations of the furnace more effectively than had been the case with the old apparatus. An alternating current Wheatstone bridge method was used for resistances up to one megohm. For greater resistances the d. c. bridge method employed in the previous investigation was unsatisfactory due to the large polarization which it produced in the crystals. Accordingly a d. c. deflection method was adopted in which a variable e.m.f. and a high sensitivity galvanometer (figure of merit 7.76×10^{-10}, resistance 500 ohms, critical damping resistance 10,800 ohms) and a reversing switch were put in series with the crystal, the e.m.f. being so regulated that the amount of current flowing in the circuit was of the order of 10^{-8} amps. For resistances between 10^5 megohms and 50 megohms, voltages from 100 to 2 volts were obtained from radio "B" batteries, and for resistances between 50 and 10 megohms the variable e.m.f. in the circuit was replaced by a potentiometer source. At resistances greater than 30 megohms, reversal of the current through the crystal usually gave equal deflections in opposite directions. Between 30 and 10 megohms the deflections were often unsymmetrical and erratic, so that the d. c. points in this range are not considered reliable. This erratic behavior is due largely to polarization, and perhaps in part to the fact that unavoidable thermal e.m.f.'s became appreciable in this range in comparison with the applied e.m.f.

A platinum–platinum-rhodium thermocouple and Weston Universal potentiometer were substituted for the two-junction chromel–alumel couple and extended Student Type potentiometer used in the previous investigation. The temperature could be

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[4] V. Seelen, *Z. Physik*, **29**, 125 (1924).

kept constant to about 0.1°. Calibration of the noble metal couple on three occasions during the investigation, at the steam point, sulfur point and melting points of potassium chloride and potassium sulfate, showed a maximum variation of 0.7° at the fixed points and an average variation of 0.3°.

Materials.—The thallous halides were prepared from an old stock of Kahlbaum's thallous acetate by precipitation with the appropriate halogen acid. The work was carried out in a dark room as the thallous halides are sensitive to light. The acids were distilled in an all-pyrex apparatus and the middle fraction was used for the precipitation. The precipitates were washed thoroughly with conductivity water, dried, fused and poured into a clean iron die. The plunger was quickly inserted into the die after the pouring, and given a light tap with a hammer to form the pellet. Very satisfactory homogeneous pellets resulted. These were kept in dark glass bottles.

The potassium salts were "reagent quality" or "c. p." stock, recrystallized in all cases twice or thrice from conductivity water.

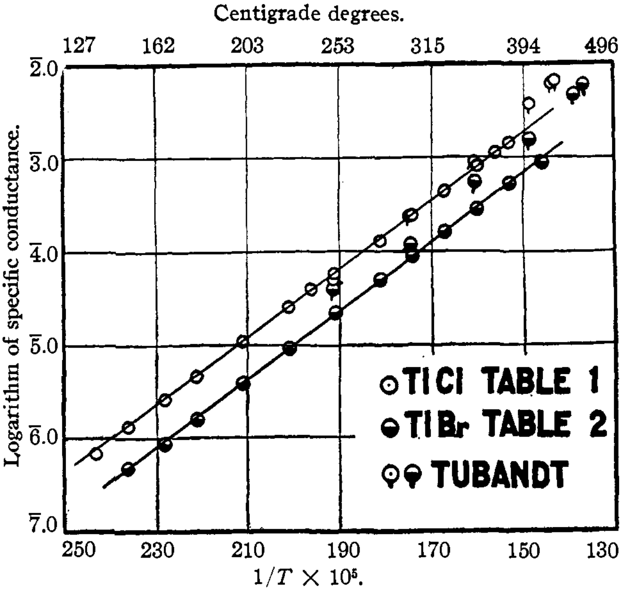

Fig. 1.—Conductance of thallous chloride and thallous bromide.

Preparation of Crystals and Pellets.—Crystals of potassium chloride and potassium bromide were grown by the method of Tammann and Veszi.[5] Visually perfect crystals from 0.5 to 1.0 cm. on edge, and 0.3 to 0.5 cm. thick were obtained. Attempts to grow crystals of potassium iodide were unsuccessful. Pellets of all the halides of potassium were made in a die with a specially hardened steel plunger at pressures of 230,000 lb. per sq. in. (16,200 kg. per sq. cm.). These pressures were somewhat higher than those applied in the case of sodium halides previously, since it was hoped that higher pressures would produce bodies which in their conduction process would approach more nearly to single crystal lattices. All three[6] halides gave translucent pellets. The bromide was more nearly transparent than the others.

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[5] Tammann and Veszi, *Z. anorg. allgem. Chem.*, **150,** 355 (1926).

[6] On account of the hygroscopic character of potassium fluoride it could not be handled satisfactorily in the present apparatus and no data for it appear here.

Experimental Results

Thallous Halides.—In Figs. 1 and 2 are plotted the data for one run on each of the halides of thallium. These curves indicate the adequacy of the log k–$1/T$ relation to represent the experimental data in these cases. For all the thallous halides the conductivity readings were very distinct and reproducible. This high degree of reproducibility is a matter of interest. It seems to indicate that polarization may depend upon lattice rigidity and may vary in degree on passing from the brittle polar salts, where restoring forces are strong, to the waxy salts where these forces are relatively weak. The change in crystal form in thallous iodide is strikingly shown in Fig. 2.

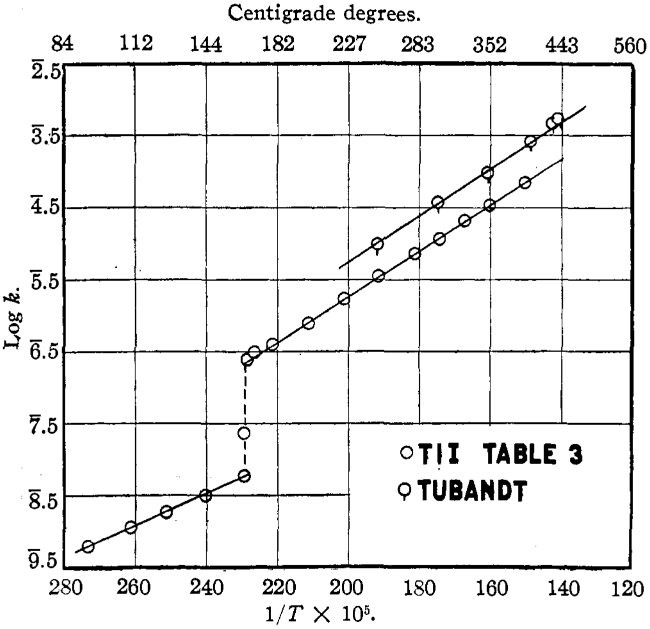

Fig. 2.—Conductance of thallous iodide.

Table I

Thallous Chloride

$1/T \times 10^5$	153	156	160	167	174	181	191
Log k	$\bar{3}.152$	$\bar{3}.045$	$\bar{4}.910$	$\bar{4}.643$	$\bar{4}.391$	$\bar{4}.110$	$\bar{5}.762$
$1/T \times 10^5$	196	201	211	221	228	236	243
Log k	$\bar{5}.585$	$\bar{5}.405$	$\bar{5}.033$	$\bar{6}.662$	$\bar{6}.408$	$\bar{6}.120$	$\bar{7}.833$

The heat of liberation calculated from the above data was 11.57×10^{-13} ergs per ion. Two other independent runs under identical conditions gave the values 11.50 and 11.38×10^{-13}. The average for the three runs was 11.48×10^{-13}.

TABLE II

THALLOUS BROMIDE

$1/T \times 10^5$	146	153	160	167	174	181
Log k	$\bar{4}.942$	$\bar{4}.718$	$\bar{4}.450$	$\bar{4}.207$	$\bar{5}.958$	$\bar{5}.701$
$1/T \times 10^5$	191	201	211	221	228	236
Log k	$\bar{5}.344$	$\bar{6}.956$	$\bar{6}.581$	$\bar{6}.201$	$\bar{7}.928$	$\bar{7}.668$

The heat of liberation from the above data was 11.68×10^{-13} ergs per ion. Another independent run gave 11.60×10^{-13}. The average was 11.64×10^{-13}.

TABLE III

THALLOUS IODIDE

$1/T \times 10^5$	150	160	167	174	181	191	201	211	221
Log k	$\bar{4}.863$	$\bar{4}.541$	$\bar{4}.326$	$\bar{4}.086$	$\bar{5}.869$	$\bar{5}.549$	$\bar{5}.243$	$\bar{6}.905$	$\bar{6}.605$
$1/T \times 10^5$	226	228	229	229	240	251	261	273	
Log k	$\bar{6}.500$	$\bar{6}.396$	$\bar{7}.375$ (a. c.)	$\bar{8}.777$ (d. c.)	$\bar{8}.512$	$\bar{8}.279$	$\bar{8}.068$	$\bar{9}.810$	

The heat of liberation from the above data for the upper slope was 10.2×10^{-13} ergs per ion and for the lower slope 6.6×10^{-13}. Two other runs under identical conditions gave for the upper slope 10.2 and 9.7×10^{-13}. The average of three runs gave for the upper slope 10.0×10^{-13}.

Potassium Halides. A. C. Values in the Transition Range.—In Fig. 3 it will be noted that the a. c. points veer off at a temperature of about 550° from the straight line upon which the high temperature points lie, and that the a. c. curve becomes almost horizontal at about 350°. Tammann and Veszi's points for potassium chloride crystal show a similar behavior. However, these investigators did not follow the curve lower than a temperature of 520°, and it is below this temperature that the anomalous behavior of the a. c. conductance values becomes most striking. A similar example of the a. c. anomaly may be seen in Fig. 5, in the case of potassium bromide crystals. A complete explanation of this behavior is lacking. It was thought at first that large high-frequency currents might be carried by a capacity effect in the crystal. However, calculation showed that the fraction of the total current which could be carried by the capacity effect (even with an assumed dielectric for the salt as great as 20) is negligibly small when 1000-cycle current is used as in the present case. The suggestion has been made that these abnormally high a. c. conductances may be explained as due to a carrying of high-frequency overtones of the alternating current by oscillation of the ions of the lattice. As lending slight experimental support to this suggestion, it may be seen that the a. c. anomaly in the transition range is less marked in the case of conglomerates (pellets) (see Figs. 4, 6 and 7) than in the case of crystals (Figs. 3 and 5). Oscillation currents would be expected to be greater in the more perfect lattice of the crystal than in the conglomerate. It is significant that the anomalous a. c. values occur in the temperature interval where we have evidence from transference numbers that the conduction process is changing from uni-ionic to bi-ionic conduction. It is possible that the impressed a. c. affects the transition from one type of conduction to the other. The conclusion of Tammann and Veszi that the log k–T relation represents the course of the conductance curve in the high temperature range better than the log k–$1/T$ relation will perhaps need to be modified if due account is taken of the a. c. anomaly.

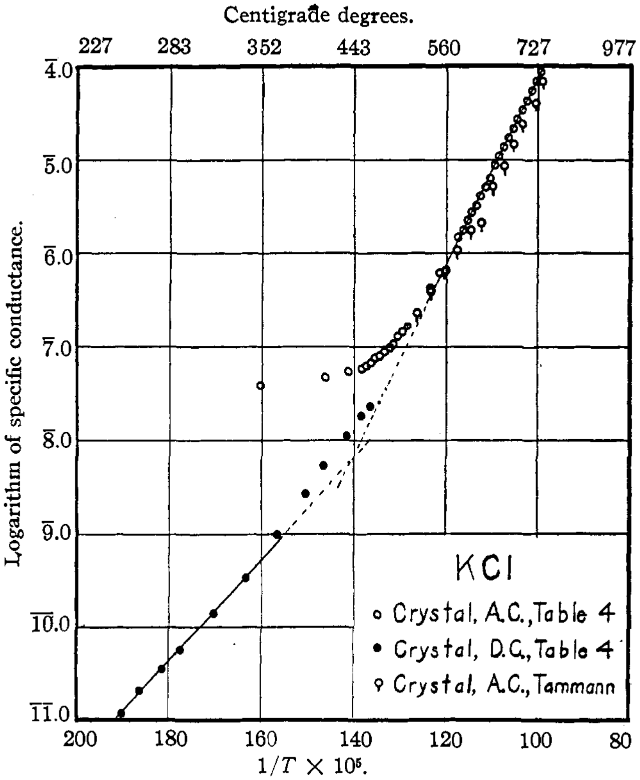

Fig. 3.—Showing (1) anomalous a. c. behavior; (2) the one-half relation between the lower and upper slopes; (3) Tammann and Veszi's crystal data.

Table IV

Potassium Chloride Crystal

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
98	$\bar{4}.057$	114	$\bar{6}.452$	138	$\bar{8}.783$
99	$\bar{5}.959$	115	$\bar{6}.357$	141	$\bar{8}.752$
100	$\bar{5}.858$	116	$\bar{6}.264$	146	$\bar{8}.685$
101	$\bar{5}.755$	117	$\bar{6}.181$	160	$\bar{8}.607$
102	$\bar{5}.650$	121	$\bar{7}.797$	191	$\overline{11}.082$
103	$\bar{5}.543$	123	$\bar{7}.632$	186	$\overline{11}.328$

TABLE IV (*Concluded*)

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
104	$\bar{5}.444$	126	$\bar{7}.368$	181	$\overline{11}.570$
105	$\bar{5}.351$	128	$\bar{7}.242$	177	$\overline{11}.771$
106	$\bar{5}.250$	129	$\bar{7}.179$	170	$\overline{10}.148$
107	$\bar{5}.151$	130	$\bar{7}.125$	163	$\overline{10}.536$
108	$\bar{5}.053$	131	$\bar{7}.041$	156	$\overline{10}.968$
109	$\bar{6}.955$	132	$\bar{7}.002$	150	$\bar{9}.442$
110	$\bar{6}.818$	133	$\bar{8}.958$	146	$\bar{9}.744$
111	$\bar{6}.724$	134	$\bar{8}.923$	141	$\bar{8}.056$
110	$\bar{6}.816$	135	$\bar{8}.889$	138	$\bar{8}.271$
112	$\bar{6}.623$	136	$\bar{8}.843$	136	$\bar{8}.368$
113	$\bar{6}.523$	137	$\bar{8}.812$		

The heat of liberation from the above data for the upper slope was 31.9×10^{-13} ergs per ion, and for the lower slope 16.0×10^{-13}. Five other runs under identical conditions gave for the upper slope 31.7, 33.0, 32.2, 32.9 and 31.1×10^{-13}, and for the lower slope 15.1 and 16.0×10^{-13}. The average of six values for the upper slope was 32.1×10^{-13}, and the average of three values for the lower slope was 15.7×10^{-13}.

TABLE V

POTASSIUM CHLORIDE PELLET

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
98	$\bar{4}.074$	131	$\bar{7}.746$	186	$\bar{9}.131$
100	$\bar{5}.861$	136	$\bar{7}.536$	181	$\bar{9}.348$
103	$\bar{5}.550$	141	$\bar{7}.346$	177	$\bar{9}.523$
106	$\bar{5}.270$	146	$\bar{7}.168$	172	$\bar{9}.751$
108	$\bar{5}.097$	206	$\overline{10}.218$	167	$\bar{9}.973$
111	$\bar{6}.860$	201	$\overline{10}.441$	162	$\bar{8}.191$
116	$\bar{6}.524$	196	$\overline{10}.679$	156	$\bar{8}.446$
121	$\bar{6}.226$	191	$\overline{10}.901$	150	$\bar{8}.699$
126	$\bar{7}.971$				

The heat of liberation from the above data for the upper slope was 30.5 and for the lower slope 14.2×10^{-13} ergs per ion. Three other runs under identical conditions gave for the upper slope 30.0, 30.3 and 30.3×10^{-13}, and another run gave for the lower slope 15.2×10^{-13}. The average of four values for the upper slope was 30.3×10^{-13}, and the average of two runs for the lower slope was 14.7×10^{-13}.

D. C. Values in the Transition Range.[7]—It will be noted in Fig. 3 that at the lowest temperatures (250–350°) the d. c. points lie upon a straight line, but between 350 and 450° they diverge considerably in the direction of conductance greater than the expected. In this transition region of temperature, namely, 350 to 500° for potassium chloride and 300–450° for potassium bromide (Fig. 5), there is probably a profound change in the conduction process. The polarization e.m.f. is no longer negligible com-

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[7] Since this account was written the treatment by Joffe [Joffe, "The Physics of Crystals," McGraw-Hill Book Co., New York, 1928, p. 75 ff.] of the polarization e.m.f. in crystals has come to the attention of the writer. Adequate data are not at hand for correcting our transition range values according to his methods. Below the transition range the polarization is undoubtedly negligible compared with the applied potential.

pared with the applied e.m.f., and the course of the curve is very uncertain throughout this range.

TABLE VI

POTASSIUM BROMIDE CRYSTAL

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
196	$\overline{12}.476$	153	$\overline{9}.138$	111	$\overline{6}.975$
193	$\overline{12}.717$	150	$\overline{9}.406$	112	$\overline{6}.890$
190	$\overline{12}.848$	146	$\overline{9}.742$	113	$\overline{6}.794$
187	$\overline{12}.988$	143	$\overline{9}.995$	114	$\overline{6}.704$
184	$\overline{11}.118$	141	$\overline{9}.290$	115	$\overline{6}.605$
181	$\overline{11}.273$	138	$\overline{8}.332$	116	$\overline{6}.514$
178	$\overline{11}.414$	102	$\overline{5}.900$	117	$\overline{6}.421$
175	$\overline{11}.577$	103	$\overline{5}.791$	118	$\overline{6}.340$
172	$\overline{11}.726$	104	$\overline{5}.687$	121	$\overline{6}.095$
169	$\overline{11}.922$	105	$\overline{5}.584$	126	$\overline{7}.772$
166	$\overline{10}.159$	106	$\overline{5}.480$	131	$\overline{7}.500$
163	$\overline{10}.460$	107	$\overline{5}.375$	136	$\overline{7}.324$
160	$\overline{10}.754$	108	$\overline{5}.274$	141	$\overline{7}.220$
160	$\overline{10}.621$	109	$\overline{5}.178$	146	$\overline{7}.168$
156	$\overline{10}.908$	110	$\overline{5}.078$		

The heat of liberation from the above data for the upper slope was 31.4×10^{-13} and for the lower slope 15.0×10^{-13}. One other run under identical conditions gave for the upper slope 31.3 and for the lower slope 15.9×10^{-13}. The average of two runs gave for the upper slope the value 31.3 and for the lower slope 15.4×10^{-13}.

TABLE VII

POTASSIUM BROMIDE PELLET

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
243	$\overline{11}.129$	188	$\overline{9}.670$	110	$\overline{5}.259$
238	$\overline{11}.382$	183	$\overline{9}.887$	111	$\overline{5}.180$
233	$\overline{11}.587$	178	$\overline{8}.093$	112	$\overline{5}.107$
228	$\overline{11}.822$	102	$\overline{4}.002$	113	$\overline{5}.036$
223	$\overline{10}.072$	103	$\overline{5}.809$	116	$\overline{6}.842$
218	$\overline{10}.305$	104	$\overline{5}.803$	121	$\overline{6}.598$
213	$\overline{10}.542$	105	$\overline{5}.708$	126	$\overline{6}.386$
208	$\overline{10}.774$	106	$\overline{5}.610$	131	$\overline{6}.204$
203	$\overline{9}.008$	107	$\overline{5}.518$	136	$\overline{6}.014$
197	$\overline{9}.278$	108	$\overline{5}.430$	141	$\overline{7}.844$
193	$\overline{9}.461$	109	$\overline{5}.344$	150	$\overline{7}.540$

The heat of liberation from the above data for the upper slope was 29.4×10^{-13} ergs per ion and for the lower slope 14.7×10^{-13}. Another run under identical conditions gave for the upper slope 29.0 and for the lower slope, 14.1×10^{-13}. The average of the two runs for the upper slope was 29.2 and for the lower slope 14.4×10^{-13}.

Differences between Conduction in Crystals and Pellets.—Figures 4 and 6 show the difference in conductance between pellets and crystals. The discrepancy is seen to be greater at lower temperatures, the pellet tending to have a slightly lesser slope. It will be noted in all of these cases that the uncertainty of the d. c. points in the transition range is less for the pellets than for the crystals. It seems to be generally true that polarization is less in the conglomerate than in the crystal. This is readily seen by comparing pellets of potassium chloride (Fig. 4) with crystals of potassium chloride (Fig. 3). In the case of the pellet the d. c. points fall regularly on a straight line to conductances greater than 10^{-8}, while in the case of the crystal there is a marked deviation even at conductances less than 10^{-9} reciprocal ohms. A second striking difference between the behavior of crystal and pellet is that the change in slope (and presumably the change in the conduction process also) occurs at a much higher temperature for the pellet than for the crystal. For example, in Fig. 3 for the crystal the intersection of the two slopes (produced) is at approximately 440°. On the other hand, in Fig. 4 for the pellet the corresponding intersection comes at a temperature of approximately 570°. Similarly for the potassium bromide crystal in Fig. 5 the intersection comes at

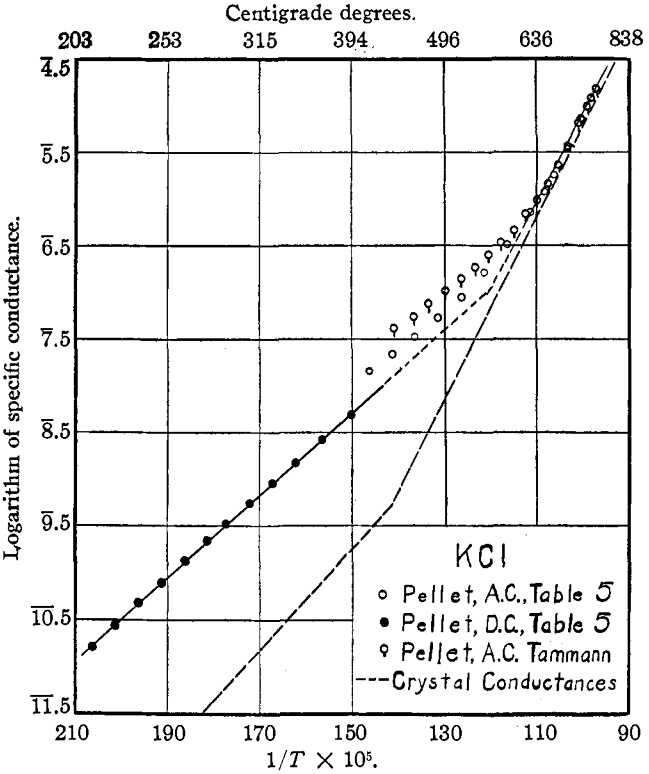

Fig. 4.—Showing (1) the higher conductance and lesser slope of pellets as compared with crystals at lower temperatures; (2) the merging of pellet and crystal data at higher temperatures; (3) Tammann and Veszi's pellet data.

approximately 370 and for the potassium bromide pellet in Fig. 6 it comes at about 600°. A third point of difference between pellet and crystal is that the heat of liberation is slightly less for the pellet than for the crystal. This is shown in Table IX. Potassium chloride crystals, for example, show values of 15.7 and 32.1 $\times 10^{-13}$ ergs/ion, calculated from the lower and upper slopes, respectively. The corresponding values for potassium chloride pellets are 14.7 and 30.3 $\times 10^{-13}$ ergs/ion.

TABLE VIII

POTASSIUM IODIDE PELLETS

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
Number 1		145	$\bar{7}.270$	109	$\bar{5}.818$
106	$\bar{5}.839$	146	$\bar{7}.212$	110	$\bar{5}.733$
107	$\bar{5}.758$	147	$\bar{7}.165$	111	$\bar{5}.648$
108	$\bar{5}.688$	148	$\bar{7}.128$	112	$\bar{5}.563$
109	$\bar{5}.608$	149	$\bar{7}.098$	113	$\bar{5}.492$
110	$\bar{5}.529$	150	$\bar{7}.078$	114	$\bar{5}.414$
111	$\bar{5}.448$	156	$\bar{8}.962$	115	$\bar{5}.348$
112	$\bar{5}.374$	201	$\overline{10}.454$	116	$\bar{5}.277$
113	$\bar{5}.301$	196	$\overline{10}.638$	117	$\bar{5}.208$
114	$\bar{5}.230$	191	$\overline{10}.832$	128	$\bar{6}.487$
115	$\bar{5}.158$	186	$\bar{9}.042$	139	$\bar{7}.840$
116	$\bar{5}.088$	181	$\bar{9}.236$	201	$\overline{10}.891$
117	$\bar{5}.024$	177	$\bar{9}.379$	196	$\bar{9}.091$
118	$\bar{6}.959$	174	$\bar{9}.500$	191	$\bar{9}.298$
119	$\bar{6}.892$	170	$\bar{9}.676$	186	$\bar{9}.502$
123	$\bar{6}.631$	167	$\bar{9}.804$	181	$\bar{9}.702$
126	$\bar{6}.440$	163	$\bar{9}.981$	177	$\bar{9}.853$
128	$\bar{6}.320$	160	$\bar{8}.176$	172	$\bar{8}.074$
131	$\bar{6}.110$	156	$\bar{8}.332$	167	$\bar{8}.277$
133	$\bar{7}.981$			162	$\bar{8}.510$
136	$\bar{7}.800$	Number 2		156	$\bar{8}.776$
139	$\bar{7}.634$	106	$\bar{4}.100$	150	$\bar{8}.998$
143	$\bar{7}.358$	107	$\bar{5}.994$	146	$\bar{7}.483$
144	$\bar{7}.311$	108	$\bar{5}.903$		

The heat of liberation from the data of Pellet No. 1 for the upper slope was 24.0 and for the lower slope, 12.5 $\times 10^{-13}$ ergs per ion. For Pellet No. 2 the upper slope gave 25.6 and the lower slope 13.0 $\times 10^{-13}$. Another run under identical conditions gave for the upper slope 27.5 and for the lower slope 15.0. The average of the three runs gave for the upper slope 25.7 and for the lower slope 13.5 $\times 10^{-13}$.

Discussion of Results

The Conduction Process.—Two slopes were found for all the halides of sodium and potassium investigated, with the exception of sodium fluoride.[8] Single slopes only were found for thallous chloride and bromide.

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[8] The anomalous behavior of sodium iodide and sodium fluoride in the neighborhood of the melting point, reported in the previous paper, is now thought to be due to impurities. Extremely pure sodium iodide and potassium iodide failed to show the sudden rise in conductance reported for sodium iodide.

Two slopes were found for thallous iodide, but in this case it is well known that the change in slope arises from a change in crystal form. In the case of all of the halides of sodium and potassium which exhibit two slopes, the upper slope is approximately double the lower slope. That the conduction at lower temperatures is due to the alkali metal ion only is shown by the transference experiment of v. Seelen[4] upon sodium chloride at 400°, and by the transference experiments of Phipps and Leslie[8] upon sodium chloride between 410 and 510°. Indirect evidence pointing to the same conclusion is seen in the work of Schmidt,[9] who found at lower temperatures that one ion only (usually the positive ion) was emitted from solid salts. At higher temperatures Schmidt found that both ions were emitted from solid salts in nearly all cases. In agreement with this, transference data now available[3] for sodium chloride between the temperatures of 558 and 655° indicate that both ions take part in the conduction process over this range of temperature. Change from uni-ionic to bi-ionic conduction is exhibited by the chlorides, bromides and iodides of both sodium and potassium. This phenomenon appears to be characteristic of, and perhaps limited to, high-melting polar salts, since it is not shown by the halides of silver, thallium or lead.

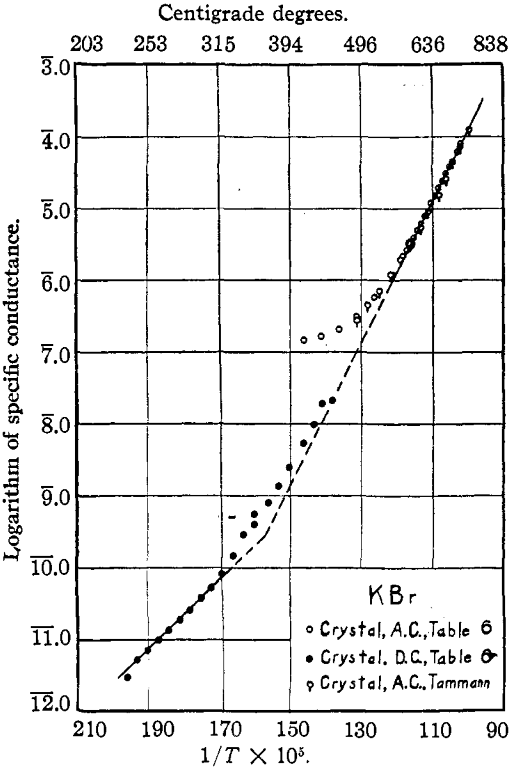

Fig. 5.—Showing (1) the one-half relation between lower and upper slopes; (2) deviation of both a. c. and d. c. points at intermediate temperatures; (3) Tammann and Veszi's crystal data.

The Adequacy of the Log k-$1/T$ Relation.—The log k-$1/T$ relation fits the data admirably in the case of the thallous halides over a range of temperature from 150° to temperatures within 30° of their melting points. In the case of the potassium halides we have already pointed out the need for caution in accepting the results of either an a.-c. or an uncorrected

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[9] G. C. Schmidt, *Ann. Physik*, 80, 588 (1926).

TABLE IX

ILLUSTRATING DIFFERENCES BETWEEN HEATS OF LIBERATION IN CRYSTALS AND IN PELLETS

Salt	Form	$\epsilon \times 10^{13}$ ergs/ion Lower slope	Upper slope
KCl	Crystal	15.7	32.1
	Pellet	14.7	30.3
KBr	Crystal	15.4	31.3
	Pellet	14.4	29.2
KI	Crystal	..	..
	Pellet	13.5	25.7

d.-c. method in the transition range where the conduction process is changing, and where polarization effects are greatest. If greater weight is given to the points in the two regions where reproducibility of measurement is the greatest, namely, to those a.-c. points which are well above the transition range, and to those d.-c. points which are well below it, the log k–$1/T$ relation is entirely adequate. The remarkable success of the log k–$1/T$ relation in the thallous series where polarization is a mini-

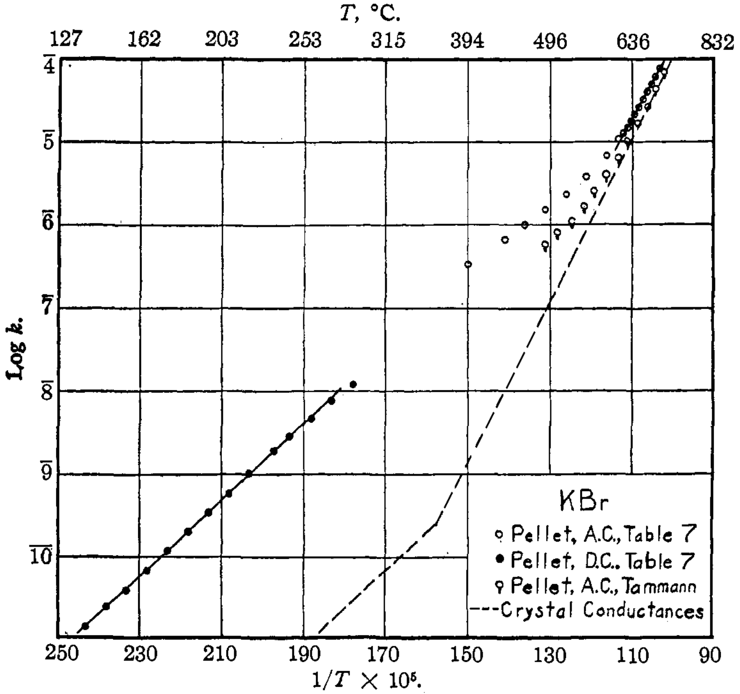

Fig. 6.—Showing (1) the one-half relation between lower and upper slopes; (2) higher conductance of pellet as compared with crystal; (3) Tammann and Veszi's pellet data.

mum and the conduction process uniform, gives us considerable confidence in its application to the less regular data of the polar salts where marked polarization accompanying the change in the conduction process has hitherto caused doubt in the choice between the log k–$1/T$ and the log k–T relation.

Heats of Liberation.—In Table X are summarized values for the heats of liberation of the halides of sodium, potassium and thallium. We may say provisionally that the values in Col. 3 are the heats of liberation of the positive ion, and the values in Col. 4 the heats of liberation of both positive and negative ions of the lattice in each case. On comparing Cols. 3 and 4 it is evident that in six cases the heat of liberation calculated from the upper slope is within experimental error double that from the lower slope. In the upper temperature range the lattice is "loosened," and whenever a positive ion of exceptional energy takes part in the conduction process it appears that a negative ion also receives the activating energy.

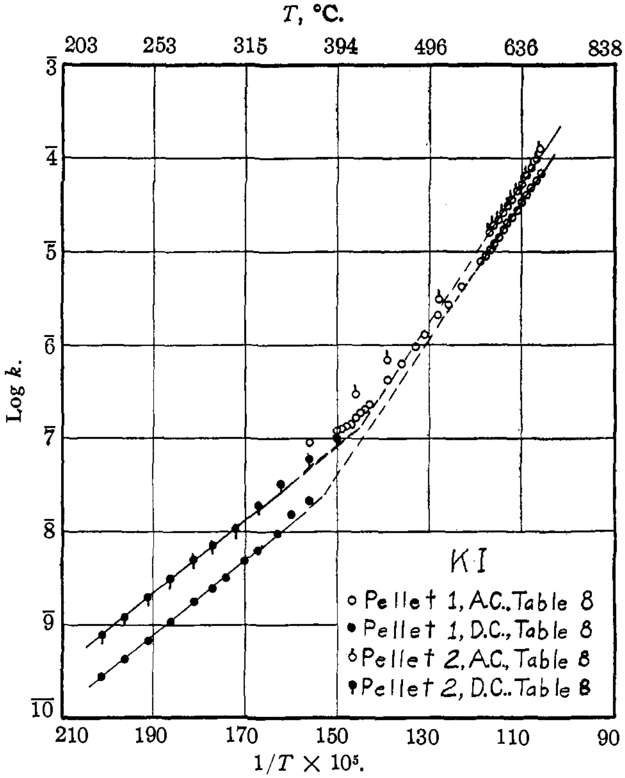

Fig. 7.—Showing (1) the one-half relation between the lower and upper slopes; (2) agreement in slope of two runs upon different pellets.

TABLE X

SUMMARY OF HEATS OF LIBERATION

Salt	M. p., °K.	ΔH, cal./g.-ion (lower slope)	ΔH, cal./g.-mole (upper slope)
NaCl	1077	20200	39800
NaBr	1028	18400	38400
NaI	924	13800	28300
KCl	1043[a]	22800	46600
KBr	1006[a]	22400	45400
KI	952[a]	19600	37200
TlCl	702[a]	16700	....
TlBr	732[a]	17000	....
TlI	713	14600	(9600)[b]

[a] Redetermined for the salts used in this investigation.

[b] Change in crystal form accounts for the existence of an upper slope in this case.

It will be noticed that the potassium ion has a larger heat of liberation than has the sodium ion in the same halide lattice, corresponding to the common conception of the potassium halides as more polar than the sodium halides. The heat of liberation in the thallous series is less than in the sodium or potassium series. Furthermore, the decrease in the heat of liberation (just as the decrease in melting point) is less in the sequence thallous chloride to iodide than the corresponding decreases in the other series. In the sodium and potassium series, heats of liberation (Col. 4) are approximately proportional to the absolute temperature of the melting point (Col. 2), within each series. In the thallous series the iodide, which changes crystal form, shows a departure from this rule.

In the study of the sodium series[2] it was shown that the ratio, heat of liberation per ion divided by the natural lattice quantum (as calculated from specific heat data), was roughly constant and had a value of about 40. A similar calculation from meager specific heat data for the potassium series gave values as follows: for potassium chloride, 51; for potassium bromide, 62; for potassium iodide, 60; average, 58. Further data are necessary before any conclusions can be drawn as to a possible relation between heat of liberation and natural quantum of the lattice.

The lattice energy of potassium chloride as calculated by Born is 163,000 cal. per gram-mole. The heat of liberation per gram-mole of potassium chloride (Col. 4, Table X) is about 47,000 cal.

Thus it appears that two oppositely charged ions which attain the threshold conduction energy in a potassium chloride lattice have less than one-third of the energy necessary to remove them completely from the lattice.

Summary

Temperature–conductance curves for the solid halides of potassium and thallium have been determined over wide temperature ranges. As in the case of the sodium halides two distinct slopes were observed for the po-

tassium salts when the data were plotted to the axes log *k* (specific conductance) *versus* $1/T$. Only one slope was observed for thallous halides except in the case of thallous iodide, which undergoes a change of crystal form. In the light of recent high-temperature transference experiments, it is concluded that in the polar lattices only the positive ion conducts at lower temperatures, but that both ions conduct at higher temperatures. Change from uni-ionic to bi-ionic conduction seems to be characteristic of, and limited to, high-melting polar salts. Heats of liberation of the conducting ions in the various lattices have been calculated from the corresponding slopes. Within the sodium and potassium series heats of liberation are proportional to the melting points.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A STUDY OF THE CALCIUM AMALGAM ELECTRODE IN DILUTE AQUEOUS SOLUTIONS[1]

BY RUSSEL JOHN FOSBINDER

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The determination of the calcium-ion activities in dilute solutions of calcium salts by the measurement of the electromotive force of a cell of the proper type is interesting for two reasons. First, the electrochemical behavior of calcium amalgams against aqueous solutions of calcium salts apparently discloses many peculiarities not exhibited by other amalgam electrodes. Second, calcium-ion concentration is a matter of considerable importance in physiological chemistry.

Byers[2] attempted to determine equilibrium conditions in a system of calcium hydroxide and sodium carbonate by means of the electromotive-force method. Neuhausen and Marshall[3] studied the electrolyte equilibrium in the blood by the use of amalgam electrodes. Lucasse[4] measured the potentials of cells with and without liquid junctions to determine transference numbers and activity coefficients of the alkaline earth chlorides. Drucker and Luft[5] made a careful and critical study of the calcium electrode in solutions of calcium. Kirk and Schmidt[6] attempted to measure the calcium-ion activities in solutions of certain protein salts but stated that their technique was entirely inadequate.

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[1] This communication is based on a thesis submitted for the degree of Doctor of Philosophy at the University of Wisconsin in 1928 under the direction of Farrington Daniels.

[2] Byers, THIS JOURNAL, **30**, 1584 (1908).

[3] Neuhausen and Marshall, *J. Biol. Chem.*, **53**, 365 (1922).

[4] Lucasse, THIS JOURNAL, **47**, 743 (1925).

[5] Drucker and Luft, *Z. physik. Chem.*, **121**, 307 (1926).

[6] Kirk and Schmidt, *J. Biol. Chem.*, **76**, 115 (1928).