

| KAsO ₂ , g. | FeSO ₄ ·7H ₂ O, g. | O ₂ abs., cc. | Calcd. for 2FeSO ₄ ·7H ₂ O, cc. |
|------------------------|--|--------------------------|--|
| 0.490 | 0.50 | 26.7 | 27.4 |
| .490 | .30 | 17.2 | 16.4 |

From these values it is readily seen that those calculated on the basis that autoxidation was taking place are in very good agreement with those actually found. Curve 2, Fig. 3, shows the rate at which absorption takes place. From the figure it is evident that this absorption curve follows very closely that of the catalyst itself, showing that we are dealing again with an autoxidation.

Summary

The present investigation was carried out to show, if possible, what the mechanism of the oxidation process is, using ferro-pyrophosphate as catalyst. The conclusion has been reached that in the oxidation of potassium arsenite and sodium ferro-pyrophosphate there is an intermediate "mol-oxide" formed, which is the active oxidizing agent. In the case of the oxidation of sodium sulfite, the mechanism can be explained either on this hypothesis or by assuming the oscillation of the iron salt between its two valences. From the shape of the absorption curve in the initial stages, however, it seems likely that here too the oxidation is by the iron "mol-oxide." These views are substantiated by quantitative measurements, and by the order of the reaction.

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

TEMPERATURE-CONDUCTANCE CURVES OF SOLID SALTS I. THE HALIDES OF SODIUM

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Temperature-conductance curves of fused salts and of solutions are difficult to interpret since both the number of ions and the ion mobilities change simultaneously with temperature. On the other hand the electrolytic conductance of a solid salt at a given temperature depends only upon the number of free ions present in the lattice at that temperature; the mobility of these ions may be assumed to be constant, at least for temperatures remote from the melting point.

The first important generalization relating temperature to the conductance of solids was made by Rasch and Hinrichsen¹ and independently by J. Königsberger.² It was observed that a linear relation resulted in all cases when $\log \kappa$ (specific conductance) was plotted against $1/T$ (the

¹ Rasch and Hinrichsen, *Z. Elektrochem.*, **14**, 41 (1908).

² Königsberger, *Physik. Z.*, **8**, 833 (1907).

reciprocal of the absolute temperature), and this doubtless suggested the applicability of the van't Hoff relation,

$$d \ln \kappa / dT = q/RT^2 \quad (1)$$

where κ is specific conductance, and q is presumably a quantity of heat. Upon integration they obtained

$$\ln \kappa = -q/RT + C' \quad (2)$$

This was written by Rasch and Hinrichsen, Joffé and others in the general form $\log \kappa = A/T + C$; q/R thus became A , which seems to have been regarded merely as a constant in a semi-empirical equation by most of the investigators of conductance in solids who came after Rasch and Hinrichsen; and the significance of the q of the original van't Hoff relation, embodied in this A , seems to have been largely lost. We may conveniently designate this q as the *heat of liberation* of a gram ion in a crystal lattice. It is the work necessary to produce a mole of gaseous ions in the interior of a crystal; or, following the nomenclature of kinetics of reactions, q may be considered as the *heat of activation* or as the *critical increment* of energy which the ions of a lattice must acquire in order to be free to take part in electrolytic conduction. To avoid the confusion which the last two terms might cause, q will be referred to below as the *heat of liberation*.

The object of this work is to accumulate accurate data upon the conductance of several typical solid electrolytes over wide ranges of temperature, to calculate the heats of liberation of the conducting ions in the different lattices, and finally to attempt a correlation between heats of liberation and the "natural quanta" of crystals, derivable from specific-heat data and other sources. This paper is confined to the accumulation of data upon the conductance of the halides of sodium, and to an attempt at interpreting their curves.

Methods

Because of the difficulty of growing large perfect crystals of sodium chloride, bromide and iodide, the method of pressing the powdered salt into disks, as used by Benrath³ and others, was adopted. Preliminary experiments upon disks of sodium chloride prepared in an ordinary hand press under relatively low pressures, showed that their specific conductance was in nearly all cases greater than that of the crystal. Furthermore the slopes of the conductance curves, while checking in some cases with the slopes obtained with crystals, were not uniformly trustworthy. Especially in the vicinity of the melting point the disk appeared to undergo a slow progressive change, probably the result of slight sintering and increase of crystal size. High pressures of about 8000 atmospheres were then applied by means of an Oleson Testing Machine in the University Laboratory of Applied Mechanics. This pressure was near the limit of strength of the

³ Benrath, *Z. physik. Chem.*, **77**, 257 (1911).

piston which was being used. Disks of sodium chloride about 1.5 mm. thick; prepared in this way, were quite transparent. Disks of sodium bromide and sodium iodide were translucent, though not transparent. Disks of sodium fluoride were only slightly translucent, even under 9,330 atmospheres' pressure. It seems likely that with a specially hardened piston and mould, still higher pressures would produce completely transparent disks, whose properties would approximate closely those of crystals. Comparison of high pressure (h. p.) sodium chloride disks with natural rock-salt crystals showed that the slopes of the conductance curves were the same, and also that the absolute agreement between values of the specific conductances at the same temperature was about as good as between two different crystals.

Materials

The sodium chloride, bromide and iodide were obtained from Professor S. A. Braley of the Analytical Division of this Laboratory, and had been twice crystallized, twice centrifuged, and dried at temperatures near their respective melting points. The sodium fluoride was the c. p. grade of Baker and Adamson, and was not further purified.

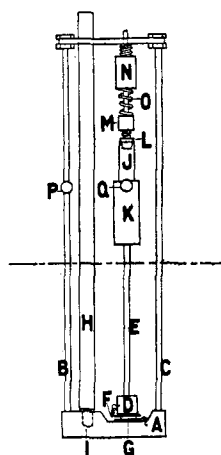


Fig. 1.—Diagram of conductance apparatus.

Apparatus.—The frame used for holding the platinum electrodes in contact with disk or crystal is a modification of the apparatus of Goodwin and Mailey.⁴ Parts A, B, C, D and E are all of nickel. F and G are heavy platinum plates interposed between the disk of salt and the nickel frame above and below, and making secure electrical connection to D and A, respectively, through flexible spirals of platinum wire, which in turn are spot-welded both to platinum plate and to nickel frame. H is a quartz tube which supports the 2-junction Chromel-Alumel couple. I is a "well" in the nickel base into which the thermocouple junctions are inserted. All of the machined parts above the dotted line (outside of the furnace) are brass. J is a transparent quartz tube insulator, securely cemented into the brass part K, and given a downward thrust by the plunger L; L is tapered so as to center itself in J and bear down evenly upon the top of J. M and N are nuts used for varying the tension in the spring O which actuates the plunger L, and for making adjustment to different thicknesses of disk below. P and Q are brass connectors hard-soldered to the frame, for leads to the conductivity bridge.

The heating was done by a Multiple Unit, Type 84, electric furnace made by the Electrical Heating Apparatus Company. A lid was specially

⁴ Goodwin and Mailey, *Phys. Rev.*, 23, 26 (1906).

constructed of heavy Transite board to fit closely around the frame without touching it. For convenience in removing, the lid was made in two sections.

Two methods have been used heretofore for securing good contact between electrodes and crystal or disk—graphitizing and platinizing. Graphitizing consisted merely in rubbing graphite powder into the two crystal faces, or more simply in "writing" all over the two surfaces with a soft pencil. Platinizing as carried out by the authors consisted in sputtering a film of platinum on to the two surfaces by the familiar method of cathode sputtering in a vacuum. Neither graphitizing nor platinizing is satisfactory at 800° since the first burns off and the second disintegrates. The final method of establishing good contact was as follows. The polished disk or crystal was clamped between the platinum electrodes with stiff compression of the spring. The frame was lowered into the furnace and the whole was heated up to a temperature within 20–30° of the melting point of the crystal. The salt sinters slightly and the force of the spring causes the disk or crystal to flow enough to form itself to the electrodes, thereby insuring perfect contact at all points. When the electrodes were separated from the disk at the end of a run, it was observed that the salt had "wet" the electrodes evenly over the whole surface of contact. The slight deformation of the disk caused by this treatment made it necessary to re-determine its dimensions at the end of a run. This was done by taking an over-all caliper of disk and electrodes with a micrometer caliper, and then subtracting the known average thickness of the two electrode plates at the region of contact with the disk. The final diameter of the disk was also determined after separation from the electrodes.

To measure the temperature a 2-junction Hoskins' Chromel-Alumel thermocouple was used. A Leeds and Northrup students' Potentiometer, extended to read to 0.01 mv., was used. Temperature differences of 20° to 50° could be read with an accuracy of 0.1°, and the actual temperature could be trusted to within 1° or 2°, as was shown by frequent recalibrations against the melting points of Bureau of Standards samples of tin, zinc, aluminum and copper. The temperature was controlled by hand, and could be kept constant to 0.1°. Temperature control was facilitated by the method of mounting disk and thermocouple in intimate contact with the large mass of metal in the nickel base.

Resistances from 0 to 0.5 megohm were measured by means of telephone and drum-wound conductivity bridge of the usual type, with a Leeds and Northrup 1000-cycle microphone hummer as the source of alternating current. Resistances from 0.5 megohm to 100 megohms were measured by the Wheatstone-bridge method described by Northrup.⁵ Eight volts

⁵ Northrup, "Methods of Measuring Electrical Resistance," McGraw-Hill Book Co., New York, 1912, p. 153.

d.c. was used in the range of lower resistances, and 110 volts d.c. for the highest resistances. There was evidence that 110 volts d.c. caused a disruption of the crystal in the range from 0.5 megohm to 10 megohms. To avoid this the following procedure was adopted in certain cases. Good contact with electrodes was secured just below the melting point of the crystal. The temperature was then decreased in steps of 20° to 50° and readings were taken until the limit of the a.c. bridge was reached. Then the temperature was lowered to the 100-megohm lower limit of the d.c. bridge, and d.c. points were taken at intervals with a rising temperature. This left the region of worst polarization and of disruptive electrolysis until the end of the run. Great difficulty was experienced in getting satisfactory readings in this range. In all cases of doubt we have weighted the points which lie well within the a.c. range and those in the lower d.c. range well removed from this transition region. No attempt was made to measure resistances greater than 100 megohms since experience showed that resistances greater than this were subject to errors due to failure of insulation.

Data and Results

Curves D and E (Fig. 2) show the $\log \kappa$, $1/T$ curves for three runs each with sodium chloride crystal and sodium chloride disk, respectively.

TABLE I
COMPOSITE DATA OF THREE EXPERIMENTS WITH DIFFERENT CRYSTALS OF SODIUM CHLORIDE (NAVARRÉ)

| $1/T \times 10^5$ | $\log \kappa$ | $1/T \times 10^5$ | $\log \kappa$ | $1/T \times 10^5$ | $\log \kappa$ | $1/T \times 10^5$ | $\log \kappa$ |
|-------------------|---------------|-------------------|---------------|-------------------|---------------|-------------------|---------------|
| 94.7 | $\bar{4}.960$ | 110.7 | $\bar{5}.380$ | 123.5 | $\bar{6}.312$ | 143.1 | $\bar{7}.148$ |
| 95.3 | $\bar{4}.850$ | 111.0 | $\bar{5}.160$ | 123.7 | $\bar{6}.244$ | 148.1 | $\bar{8}.921$ |
| 95.0 | $\bar{4}.752$ | 114.8 | $\bar{6}.992$ | 126.0 | $\bar{6}.078$ | 153.0 | $\bar{8}.760$ |
| 97.0 | $\bar{4}.673$ | 116.0 | $\bar{6}.760$ | 126.5 | $\bar{7}.877$ | 156.1 | $\bar{8}.517$ |
| 98.0 | $\bar{4}.421$ | 117.5 | $\bar{6}.815$ | 126.0 | $\bar{7}.908$ | 167.0 | $\bar{8}.215$ |
| 99.3 | $\bar{4}.370$ | 120.9 | $\bar{6}.493$ | 128.2 | $\bar{7}.924$ | 168.2 | $\bar{9}.998$ |
| 101.0 | $\bar{4}.125$ | 121.0 | $\bar{6}.438$ | 132.1 | $\bar{7}.637$ | 174.7 | $\bar{9}.746$ |
| 103.1 | $\bar{4}.070$ | 121.0 | $\bar{6}.275$ | 133.0 | $\bar{7}.527$ | 179.5 | $\bar{9}.619$ |
| 106.0 | $\bar{5}.614$ | 122.6 | $\bar{6}.329$ | 136.3 | $\bar{7}.503$ | 179.6 | $\bar{9}.548$ |
| 109.3 | $\bar{5}.487$ | | | 141.0 | $\bar{7}.215$ | | |

TABLE II
COMPOSITE DATA OF THREE RUNS WITH DIFFERENT HIGH-PRESSURE DISKS OF SODIUM CHLORIDE

| $1/T \times 10^5$ | $\log \kappa$ | $1/T \times 10^5$ | $\log \kappa$ | $1/T \times 10^5$ | $\log \kappa$ | $1/T \times 10^5$ | $\log \kappa$ |
|-------------------|---------------|-------------------|---------------|-------------------|---------------|-------------------|---------------|
| 94.8 | $\bar{4}.843$ | 103.0 | $\bar{4}.022$ | 128.9 | $\bar{6}.135$ | 153.0 | $\bar{8}.950$ |
| 95.0 | $\bar{4}.702$ | 106.0 | $\bar{5}.663$ | 131.0 (A.C.) | $\bar{7}.976$ | 156.1 | $\bar{8}.653$ |
| 95.0 | $\bar{4}.707$ | 111.0 | $\bar{5}.254$ | 131.0 (D.C.) | $\bar{7}.879$ | 160.0 | $\bar{8}.643$ |
| 97.0 | $\bar{4}.610$ | 111.0 | $\bar{5}.238$ | 136.0 | $\bar{7}.724$ | 167.0 | $\bar{8}.326$ |
| 98.0 | $\bar{4}.396$ | 111.6 | $\bar{5}.240$ | 139.9 | $\bar{7}.460$ | 169.1 | $\bar{8}.088$ |
| 98.0 | $\bar{4}.406$ | 116.0 | $\bar{6}.898$ | 141.0 | $\bar{7}.494$ | 174.0 | $\bar{8}.001$ |
| 100.0 | $\bar{4}.306$ | 116.0 | $\bar{6}.864$ | 144.7 | $\bar{7}.300$ | 181.0 | $\bar{9}.716$ |
| 101.0 | $\bar{4}.132$ | 120.0 | $\bar{6}.632$ | 144.7 | $\bar{7}.396$ | 181.0 | $\bar{9}.634$ |
| 100.0 | $\bar{4}.130$ | 121.0 | $\bar{6}.537$ | 146.0 | $\bar{7}.262$ | | |

Tables I and II give the composite data of these six runs, from which Curves D and E were constructed. At the value $1/T \times 10^5 = 128$ ($t = 508^\circ$), the slope for the crystal increases. The corresponding change for the disk occurs at 543° . The upper and lower slopes parallel each other closely, and the upper slope is twice the lower slope within experimental error. The change in slope is not quite as abrupt as Curves D and E seem to indicate. There is a tendency for the two slopes to slur more gradually into each other. The transition is not sharp, but if one passes through this region *very slowly* the two slopes become quite distinct, and with long waiting approach the ideal shown in D and E.

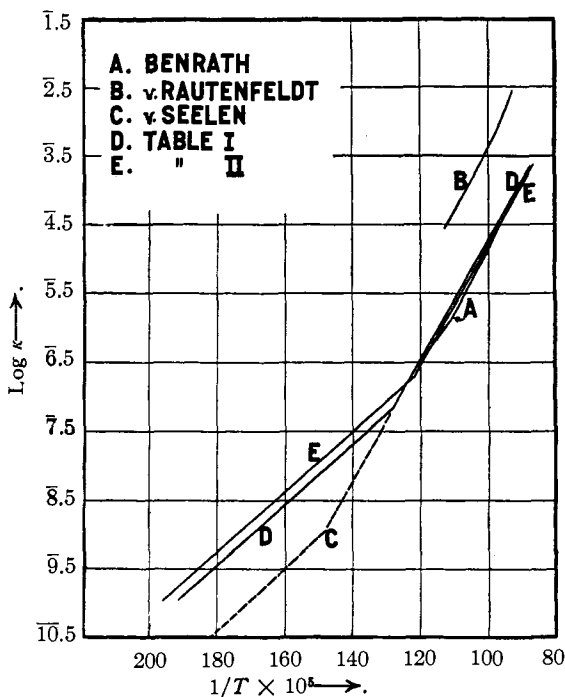


Fig. 2.—The conductance of NaCl.

Curve C gives v. Seelen's slopes⁶ in this temperature range. They are nearly identical with the slopes of D and E, but the change in slope occurs at a much lower temperature, approximately 412° . This discrepancy is probably to be explained by differences in the method of making contact, by differences in temperature treatment before the run, or by differences in exclusion of radiation from without the furnace. V. Rautenfeldt's⁷ data (Curve B) are clearly in error. Benrath's data (Curve A) lie below

⁶ v. Seelen, *Z. Physik*, 29, 125 (1924).

⁷ v. Rautenfeldt, *Ann. Physik*, 72, 617 (1923). A recent correction by v. Rautenfeldt [*Ann. Physik*, 75, 848 (1924)] brings his data into good agreement with ours.

Curve E between 600° and 700°, but converge toward and become identical with Curve E at temperatures both above and below this range.

Near the melting point, in the range between 750° and 800° the conductance becomes greater than is to be expected from the slopes of D and E, and the points lie slightly above these slopes. This effect is probably due to incipient melting of parts of the lattice, and is quite distinct from the change in slope mentioned above which occurs in the vicinity of 500°. V. Seelen attributed this lower change in slope to anomalous behavior due to approach to the melting point or to experimental error. However, one would not expect to meet with such behavior at 412° (v. Seelen's transition value), nearly 400° below the melting point. Undoubtedly, this lower change in slope requires a different explanation, which will be discussed below.

The data on high-pressure disks of sodium iodide and sodium fluoride are given in Tables III and IV, and the corresponding graphs are A and C of Fig. 3. A set of data taken upon a low-pressure sodium fluoride disk is also included in Table IV, and is plotted as Curve B of Fig. 3. Just as in the case of sodium chloride, sodium iodide shows two distinct slopes, *ab* and *bc* (Curve A, Fig. 3). Both slopes are less than the corresponding sodium chloride slopes, but as before the upper slope *bc* is approximately twice the lower slope *ab*. The inflection point *b* is at a temperature of about 360°. As in the case of sodium chloride, there is also a turning upward of

TABLE III

DATA OF A SINGLE EXPERIMENT WITH A HIGH-PRESSURE DISK OF SODIUM IODIDE

| $1/T \times 10^5$ | Log κ | $1/T \times 10^5$ | Log κ | $1/T \times 10^5$ | Log κ | $1/T \times 10^5$ | Log κ |
|-------------------|--------------|-------------------|--------------|-------------------|--------------|-------------------|--------------|
| 110.0 | 2.455 | 121.0 | 4.416 | 141.0 | 5.139 | 174.0 | 7.549 |
| 112.0 | 2.455 | 122.9 | 4.258 | 146.0 | 6.732 | 183.4 | 7.242 |
| 114.3 | 2.455 | 126.0 | 4.044 | 153.0 | 6.392 | 191.0 | 7.012 |
| 116.0 | 4.806 | 131.0 | 5.718 | 160.0 | 6.049 | 202.3 | 8.703 |
| 117.5 | 4.665 | 136.0 | 5.426 | 168.2 | 7.722 | 210.0 | 8.500 |
| | | | | | | 227.2 | 9.980 |

TABLE IV

SODIUM FLUORIDE

DATA OF AN EXPERIMENT WITH A
LOW-PRESSURE DISKDATA OF AN EXPERIMENT WITH A
HIGH-PRESSURE DISK

| $1/T \times 10^5$ | Log κ | $1/T \times 10^5$ | Log κ | $1/T \times 10^5$ | Log κ | $1/T \times 10^5$ | Log κ |
|-------------------|--------------|-------------------|--------------|-------------------|--------------|-------------------|--------------|
| 89.4 | 1.09 | 114.3 | 5.63 | 80.5 | 2.029 | 114.3 | 6.914 |
| 91.5 | 1.05 | 120.9 | 5.06 | 83.0 | 3.717 | 116.0 | 6.798 |
| 93.6 | 1.02 | 128.2 | 6.57 | 86.0 | 3.537 | 121.0 | 6.442 |
| 98.1 | 2.94 | 135.5 | 6.10 | 87.8 | 3.498 | 126.0 | 6.062 |
| 103.0 | 2.86 | 143.7 | 7.60 | 87.8 | 3.308 | 131.0 | 7.663 |
| 105.6 | 3.45 | 155.0 | 8.73 | 89.0 | 4.884 | 136.0 | 7.338 |
| 108.5 | 4.13 | 162.1 | 8.13 | 92.0 | 4.662 | 146.0 | 8.627 |
| 111.0 | 5.84 | 175.7 | 9.26 | 101.0 | 5.896 | 153.0 | 8.132 |
| | | | | 106.0 | 5.541 | 167.0 | 9.175 |
| | | | | 111.0 | 5.156 | | |

the upper slope *bc* as the melting point is approached. But, unlike the sodium chloride, at a temperature of 600° , which is about 60° below its melting point, the conductance rapidly increases by about 35-fold (*de*) and reaches a "shelf" (*ef*) where the temperature coefficient is practically zero. The highest temperature reached was about 640° . Whether another change in slope occurs between 640° and the melting point was not determined. When cooled, the disk was found to have nearly its original dimensions, so that the 35-fold increase in conductance was not due to premature melting of the sodium iodide.

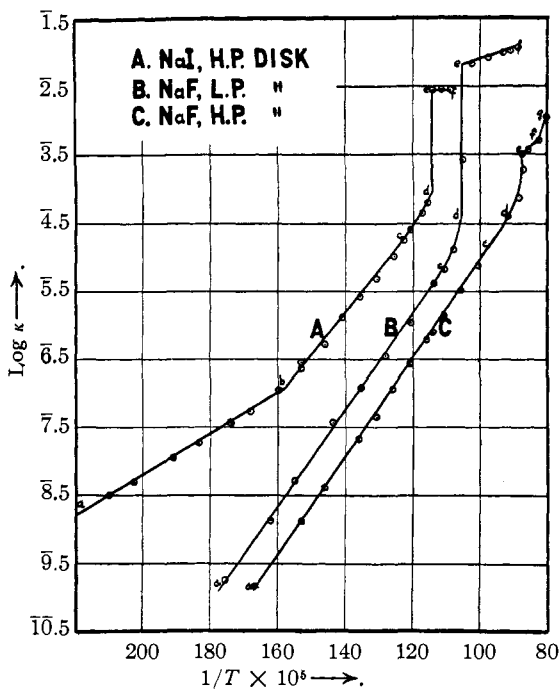


Fig. 3.—The conductances of NaI and NaF.

The behavior of sodium fluoride is unique in several respects. Considering first the low pressure disk (Curve B, Fig. 3) it is seen that from 300° up to 640° it shows only a single long slope, *ac*, and not the two slopes which characterize the other sodium halides. Between 640° and 675° (*cd*) the curve turns upward, and at 675° the conductance increases 225-fold (*de*), and reaches a slope *ef*, where the temperature coefficient is very small. This change is not instantaneous; perhaps 30 minutes elapsed between *d* and *e*.

The graph of the high-pressure disk lies below that of the low-pressure disk. It has been pointed out by v. Hevesy⁸ that the electrical conduct-

⁸ v. Hevesy, *Z. Physik*, 10, 80 (1922).

ance of a granular conglomerate is greater than that of a crystal. In this case the high-pressure disk undoubtedly approaches a crystal in its conductance, as was shown for sodium chloride in Fig. 2, and hence shows a lower conductance than the low-pressure disk, which more nearly resembles a conglomerate. Curve C shows the long slope *ac*, identical with that of B except that now it persists to a much higher temperature (about 800°). At 800° the curve begins to turn up (*cd*), and *very slowly* increases its conductance until the point *e* is reached. There is the semblance of a "shelf" between *e* and *f*, similar to that in Curve B, and finally an increase

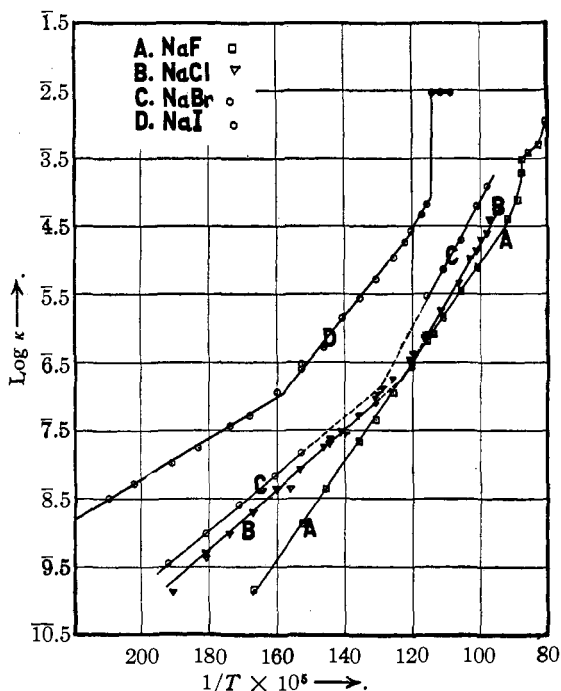


Fig. 4.—The conductances of high pressure disks of the sodium halides.

to *g* at a temperature just below the melting point. The changes which occur in the high-pressure disk are very much slower than those in the low-pressure disk. The upper course of Curve C would probably be more regular if the points were taken very slowly. At least it is apparent that the high-pressure disk is undergoing very slowly and at a higher temperature the change which occurs rapidly and at a lower temperature in the low-pressure disk.

The data for a single run made upon a high-pressure disk of sodium bromide are given in Table V and are plotted as Curve C, Fig. 4. Two slopes appear as for sodium chloride and sodium iodide. The change occurs at a

temperature of about 500°, slightly lower than for sodium chloride. Both slopes are somewhat less than those found for sodium chloride, but as in the case of the chloride the upper slope is approximately twice the lower. The similarity between sodium bromide and sodium chloride is very striking.

TABLE V

DATA OF A SINGLE EXPERIMENT WITH A HIGH-PRESSURE DISK OF SODIUM BROMIDE

| | | | | | | |
|----------------------|---------------|---------------|---------------|---------------|---------------|--------------|
| $1/T \times 10^5$ | 98.0 | 101.0 | 106.0 | 111.0 | 116.0 | ^a |
| $\log \kappa$ | $\bar{3}.082$ | $\bar{4}.782$ | $\bar{4}.293$ | $\bar{4}.858$ | $\bar{5}.464$ | |
| $1/T \times 10^5$ | 153.0 | 160.9 | 171.5 | 181.0 | 192.3 | |
| $\text{Log } \kappa$ | $\bar{7}.159$ | $\bar{8}.829$ | $\bar{8}.409$ | $\bar{9}.998$ | $\bar{9}.551$ | |

^a The minimum in the telephone for points in the lower a.c. range was broad and unsatisfactory, probably on account of inductance and capacity effects, and these points were discarded.

Discussion

A. The Form of the Temperature-Conductance Curves

The question at once arises as to which ion is conducting. The work of Tubandt⁹ has shown that in most cases the positive ion is the electrolytic carrier. A notable exception is plumbous chloride where only the chloride ion conducts. More recently, v. Seelen⁶ has shown very ingeniously that in sodium chloride at 400°, the sodium ion conducts all of the current. V. Seelen also determined the slope of the $\log \kappa$, $1/T$ curve for sodium chloride and found it to be linear between room temperature and 400°. Hence we may conclude that *the lower slopes* in the case of all the sodium halides give the heats of liberation of the *sodium ion* in the respective lattices. There is room for question in the anomalous case of sodium fluoride, but in the absence of evidence to the contrary we shall assume that sodium ion is also the conducting ion in that case.

We may inquire next concerning the significance of the upper range where the slope appears to be very nearly double the lower slope in three cases. We have no experimental basis for answering this. No transference experiments, so far as the authors know, have been undertaken above 500° to determine whether or not the negative ion also begins to conduct in sodium chloride in the higher temperature range. Thermal diffusion would doubtless interfere very seriously with transference experiments at high temperatures. The speculation is rather near to hand that in the upper range *both ions conduct simultaneously*. It is very significant in connection with this speculation that sodium fluoride with melting point at 992° should show the same slope at 800° as at 300°, that is, that sodium ion should be conducting over a range much greater than for the other halides of lower melting point. The rigidity of the fluoride lattice, as evidenced by the high melting point and high "characteristic temperature"¹⁰

⁹ Tubandt, *Z. anorg. allgem. Chem.*, **115**, 105 (1921).

¹⁰ The temperature at which $C_v = 3R/2$.

would make simultaneous conduction by fluoride ion and sodium ion highly improbable at lower temperatures. The most plausible assumption is that the fluoride ion takes no part in conduction below 800° .

We may inquire next as to the abnormal increase in conductance of sodium iodide and sodium fluoride at temperatures still considerably below their respective melting points. Two explanations suggest themselves. (1) A change in crystal form occurs, similar to that observed by Tubandt¹¹ in the case of silver iodide, which changes at about 144° from hexagonal to simple cubic form. Indeed when the data of Tubandt are plotted to the $\log \kappa$, $1/T$ axes, the graph shows a general form quite like that of sodium iodide and sodium fluoride (low-pressure disk), namely, a normal slope, a sudden vertical rise, and finally a flat "shelf." (2) Without changing crystal form, one-half of the lattice "melts" while the other half maintains the form of the lattice. This would explain the very small temperature coefficient in the higher range, since the conducting half of the lattice would in effect be a melt and would show the relatively low temperature coefficient of a melt. In the case of sodium fluoride one might expect the sodium of the lattice to "melt" first. If at 800° only sodium ion conducts in sodium fluoride, and if above 800° the sodium of the lattice "melts," one would expect exactly the type of curve found experimentally, namely, a single long slope (without the break found in the other halides) up to 800° , and then a rapid rise to a "shelf." Very close to the melting point the negative ion might begin to conduct, and we should expect the very steep slope fg (Curve C, Fig. 3), as is realized experimentally.

In the case of sodium iodide, the iodide ion conducts simultaneously with the sodium ion from a temperature as low as 360° up to 600° before the phenomenon of "half-melting" occurs. It is conceivable that the iodide lattice might melt first in this case, but since sodium ion conducted at temperatures lower than did the iodide ion, the presumption is in favor of sodium undergoing the half-melting here as in the case of sodium fluoride.

The first and second explanations offered above are not necessarily self-exclusive. In the case of silver iodide perhaps both phenomena occur together. In the change from hexagonal to simple cubic form the silver ions acquire a freedom approaching that in a melt (at least as far as the conduction process is concerned), and the conductance is actually greater than that in the melt, since the iodide ions are still in lattice alignment, and do not hinder the movement of the silver ions as much as they would in molten silver iodide. As an argument against the theory that a change in crystal form occurs may be cited the very great difference between the temperatures at which the high-pressure disk and the low-pressure disk acquire large conductances. While transitions in solids are not always

¹¹ Tubandt, *Z. physik. Chem.*, **87**, 523 (1914).

sharp,¹² we are hardly prepared to find a difference of 125° between the temperatures of transition of a high pressure and a low pressure sample of the same salt, as is the case for sodium fluoride (Fig. 3, Curves B and C). It seems more likely that the change is one which affects only the conducting ion, and not the crystal form of the lattice. Undoubtedly the environment of a conducting ion is profoundly affected by the state of compression of the salt.

The failure of sodium chloride and sodium bromide to show this many fold increase in conductance in the neighborhood of the melting point is worthy of notice. If such a change occurs in these salts, it is within less than 20° of their melting points. This region was not explored in this investigation.

B. Energy Relations

Equation 2 in the Introduction may be derived quite simply from considerations of statistical mechanics. If the assumption is made that the conductance in a solid at temperatures remote from its melting point is proportional only to the number of ions which have more than a certain threshold energy, the "free" ions—it follows from the Maxwell-Boltzman Distribution Law that $\kappa = C e^{-\epsilon/kT}$, where κ is the specific conductance, and ϵ the threshold energy or heat of liberation. This may be written in differential form as $d \ln \kappa / d(1/T) = -\epsilon/k$, or

$$\epsilon = -3.16 \times 10^{-16} \times (d \log \kappa) / (d 1/T) \text{ ergs/ion} \quad (3)$$

The heat of liberation of the conducting ion in ergs can be calculated from (3) by multiplying the slope of the $\log \kappa, 1/T$ curve by the constant -3.16×10^{-16} . This we have done in Table VI for the slopes shown in Fig. 4.

TABLE VI
RELATION BETWEEN THE HEAT OF LIBERATION OF AN ION AND THE NATURAL QUANTUM OF THE LATTICE

| Substance | $\epsilon \times 10^{18}$ (ergs) | E (cals.) | θ °K. | $h\nu_0 \times 10^{18}$ (ergs) | $\epsilon_1/h\nu_0$ | $\epsilon_2/h\nu_0$ |
|-----------|----------------------------------|-------------|--------------|--------------------------------|---------------------|---------------------|
| NaF | 22.6 | 32800 | 107 | 0.591 | 38.2 | |
| NaCl | 13.9 ^a | 20200 | 69.2 | .382 ^b | 36.4 | |
| | 27.5 | 39800 | 69.2 | .382 ^b | | 72.0 |
| NaBr | 12.7 | 18400 | 54.3 | .299 | 42.4 | |
| | 26.5 | 38200 | 54.3 | .299 | | 88.4 |
| NaI | 9.5 | 13800 | 44.7 | .247 | 38.5 | |
| | 19.5 | 28200 | 44.7 | .247 | | 79.0 |
| | | | | | Av. 38.9 | 79.8 |

^a The first ϵ value for each substance was calculated from the lower slope and is designated as ϵ_1 in Col. VI.

^b The natural quantum for sodium chloride as calculated from Ruben's residual ray frequency is 0.3808×10^{-18} ergs. Residual ray frequencies for the other sodium halides are not available.

¹² Nernst has pointed out [*Ann. Physik*, [4] **36**, 428 (1911)] that silver iodide shows an abnormal increase in specific heat near its transition point.

Col. 2 gives the heat of liberation in ergs per ion of the conducting ion as calculated from Equation 3. Col. 3 gives the heat of liberation in calories per gram ion. Col. 4 gives the characteristic temperature for each of the sodium halides. For sodium chloride the value calculated by Lewis and Gibson¹³ and for sodium bromide and sodium iodide the values calculated by Latimer¹⁴ from Koref's¹⁵ data were employed. The value for sodium fluoride was calculated by the method of Lewis and Gibson from the data of Koref. Col. 5 gives the $h\nu_0$ values as calculated from the relation

$$h\nu_0 = k \times 4.02 \times \theta \quad (4)$$

where ν_0 is the natural frequency of the atom in the lattice, h and k are the constants of Planck and of Boltzman, and θ the characteristic temperature. It follows from Equation 4 that the natural quantum of the crystal is independent of the temperature. Equation 4 follows from the Debye equation for the specific heat of a monatomic solid, which corresponds very closely with the experimental curve.¹⁶ The Debye equation gives the specific heat of monatomic solids, and its application to a binary compound, which is made up of dissimilar atoms, is open to some question. However, as shown by Lewis and Gibson¹³ using the data of Nernst and Lindemann, sodium chloride, potassium chloride and potassium bromide all conform satisfactorily to the general $C_v, \log T$ curve of Class I substances, and may be considered therefore as essentially "monatomic" with respect to the lattice forces which determine the natural frequency and the specific heat. In making the above calculation of $h\nu_0$ we assume that the halides of sodium are all "monatomic" solids.

Col. 6 gives the ratio of ϵ_1 to $h\nu_0$, and Col. 7 gives the ratio of ϵ_2 to $h\nu_0$ (ϵ_1 and ϵ_2 refer respectively to the lower and the upper slopes). The number of quanta which a sodium ion in a sodium halide lattice must acquire in order to be free to conduct is seen to be about 40. If our supposition as to the upper slope is correct, namely that in this region *both ions* take part simultaneously in the conduction, ϵ_2 is to be interpreted as the simultaneous heat of liberation of a sodium and a halide ion. That ϵ_2 should be double ϵ_1 was predictable from the fact that these salts behave like "monatomic solids" in which the two atoms are under equal constraints.

From these preliminary results we may predict that any sodium salt whose specific heat conforms to that of Class I substances will have a heat of liberation of about $40 \times h\nu_0$, where $h\nu_0$ is the natural quantum of the lattice. Perhaps this will apply to all Class I substances. Accurate

¹³ Lewis and Gibson, *THIS JOURNAL*, **39**, 2573 (1917).

¹⁴ Latimer, *ibid.*, **43**, 821 (1921).

¹⁵ Koref, *Ann. Physik*, [4] **36**, 58 (1911).

¹⁶ For a discussion of the Debye equation, see Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., 1924, vol. II, p. 1157 (Chapter XVII by W. H. Rodebush).

conductance data for testing this relation in other cases are rather meager. The data of Tubandt¹¹ upon the conductance of halides of silver and thallium have been re-plotted as above and the ϵ values determined from the slopes, with the following results. For silver chloride and thallium chloride the $\epsilon \times 10^{13}$ value is about 13.3, very nearly that obtained for sodium chloride. For silver bromide and thallium bromide the ϵ values are 12.8 and 13.3, respectively, about the same as for sodium bromide. For silver iodide the data are very meager and also unreliable on account of being taken just below the transition temperature. For thallium iodide ϵ is 10.7, which is somewhat higher than for sodium iodide, but agreeing, probably, within experimental error.

From this we may predict that in any series of uni-univalent halides, for example, chlorides of thallium, silver, sodium, etc., in which the positive ion is the conducting ion, the slopes of the conductance curves will be the same, signifying that the energy necessary to liberate any univalent ion in a chloride lattice is the same. On the other hand, in a series of univalent halides with common cation, such as sodium fluoride, chloride, bromide, iodide, etc., the slopes of the conductance curves become progressively less in the order given, signifying that the energy necessary to liberate sodium ion from a halide lattice becomes less, the greater the atomic weight of the halogen ion. However, *as the heat of liberation decreases the quantum of energy decreases correspondingly, so that the number of quanta required to activate the sodium ion is approximately constant for such a series.*

This work is being extended to other uni-univalent series, and to other valence types. Transference experiments with sodium chloride at temperatures above 500° are also being undertaken to determine whether or not chloride ion as well as sodium ion conducts in this upper range, as was assumed in part of the above discussion.

Summary

The electrical conductance of the halides of sodium in the solid state was measured over a wide range of temperatures. The powdered crystals were compressed under high pressure to semi-transparent disks. In the case of sodium chloride, the conductance of this disk agreed very well with that of a natural crystal.

A relation between the slope of the $\log \kappa, 1/T$ curves and the work of liberating an ion from the lattice was developed, and values for this work were calculated.

It was found that the work of liberating an ion is closely related to the natural quantum of the crystal as derived from specific-heat data.