The Electrical Conductivities of Molten Bismuth Chloride,

Bismuth Bromide, and Bismuth Iodide at High Pressure[1]

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(Received March 27, 1969)

The electrical conductivities of molten $BiCl_3$, $BiBr_3$, and BiI_3 were measured at temperatures up to 886° at a pressure of 5.4 kbars. At this elevated pressure the specific conductivity ($\varkappa$) varies exponentially with $1/T$, *i.e.*, $\varkappa \propto e^{-E_\varkappa/RT}$.   This is in contrast to the behavior of these molten salts at low pressures ($P < 0.1$ kbar) where Grantham and Yosim (1963) found a maximum in $\varkappa$ vs. T curves.   The isothermal electrical conductivity of molten $BiCl_3$, $BiBr_3$, and BiI_3 was examined at pressures from 3 to 14 kbars.   At temperatures above the temperature of maximum conductivity at ordinary pressures, $\varkappa$ increases with increasing pressure.   It is concluded that pressure inhibits the association of these salts at high temperature.   This effect is predominant over the decreased conductivity expected from the lower ionic mobility in liquids at these elevated pressures.

Introduction

Negative temperature coefficients of specific electrical conductivity have been reported for the bismuth salts $BiCl_3$[2a,b], $BiBr_3$[2a], and BiI_3.[2a] Negative coefficients have also been found in molten HgI_2,[3] $InCl_3$[4] and $InBr_3$.[4] This behavior of these salts has been considered anomalous, but other work by Grantham and Yosim[5] has shown that many molten salts which show conventional positive temperature coefficients near the melting point, exhibit negative temperature coefficients if their conductivities are measured over a wide enough temperature range.   Since in the conductivity measurements of Grantham and Yosim[2a,b,5] the samples expanded while they were heated, a simultaneous variation of temperature and volume took place.   These authors point out that this negative temperature coefficient probably arises due to increased covalency or ionic association of the molten salt as a result of the increased volume rather than just increased temperature.   The reduction in the number of ionic carriers offsets the increase in ionic mobility with increased temperature to give a negative temperature coefficient of conductivity at high temperatures.[5]

Measurement of the electrical conductivity at constant volume over a wide range of temperatures, particularly at temperatures where the molten salts exhibit a negative temperature coefficient of conductivity, would be useful towards a better understanding of ionic transport in these bismuth halides.   If Grantham's and Yosim's explanation of the conductivity maximum were correct, one would not expect maxima when these salts are heated at constant volume.

Estimates from thermal expansion of the liquid at pressures near atmospheric[6-8] and the compressibility of the solid[9] indicate that pressures up to 25 kbars would be required to maintain constant volume of the liquid as the temperature is raised to as much as 300° above the melting point.   Neither the experimental apparatus nor the *PVT* data are currently available with which to carry out constant volume conductivity measurements on these salts over such a pressure and temperature interval.   We have, however, made the following measurements in order to better understand the conduction process in these molten salts.   Electrical conductivities were determined as a function of temperature at a constant but relatively high pressure of 5.4 kbars.   Thus, if there is an increase in specific volume of the salt as a result of ionic association,[10,11] then such extreme pressures would be expected to decrease this association[12] and thus displace or eliminate the negative temperature

(1) This work was supported by the Research Division of the U. S. Atomic Energy Commission and was presented in part at the Pacific Conference on Chemistry and Spectroscopy, Third Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Nov. 1, 1967.

(2) (a) L. F. Grantham and S. J. Yosim, *J. Phys. Chem.*, **67**, 2506 (1963); (b) L. F. Grantham and S. J. Yosim, *ibid.*, **72**, 762 (1968).

(3) I. K. Delimarskii and B. F. Markov, "Electrochemistry of Fused Salts," Sigma Press, Washington, D. C., 1961, pp 12, 15.

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(8) F. J. Keneshea, Jr., and D. Cubicciotti, *ibid.*, **63**, 1472 (1959).

(9) A. J. Darnell and B. B. Owens, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 51V.

(10) W. Fischer, K. Heinzinger, W. Herzog, and A. Klemm, *Z. Naturforsch.*, **17a**, 799 (1962).

(11) H. A. Levy and M. D. Danford in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 109–125.

(12) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworth and Co., Ltd., London, 1957, pp 141–144.

coefficient of electrical conductivity which has been observed in these salts at relatively low pressures.[2] In addition the effect of pressure on the isothermal electrical conductivity of these molten salts was examined. Temperatures above the temperature of maximum conductance exhibited by the salts at pressures near the salts' own vapor pressures were selected for these isothermal studies. The molten salts examined in this study were subjected to a pressure variation of approximately 10 kbars. This pressure variation should, by comparison with the compression of the solid salts,[9] be sufficiently large to change the specific volume of the molten salts from 5 to 15%. Such a volume change would in all likelihood affect the conduction by an amount great enough to be detected by our high-pressure experimental technique.

The bismuth trihalides were selected for these high-pressure, high-temperature conductivity studies because (a) of their unusual conduction properties at low pressures,[2a,b] (b) their relatively low melting temperatures probably offer less experimental containment problems than would salts with higher melting points, and (c) resistance ratio measurements upon molten BiI$_3$ indicated that the temperature coefficient is normal or positive at elevated pressures.[13] The pressure-temperature dependence of the melting point and, thus, the extent of the liquid range is known.[13]

Experimental Section

A. *Materials.* Reagent grade salts were purified by multiple distillation and sublimation under vacuum and under a partial pressure of oxygen. These purified salts were loaded into the conductivity cells in an argon atmosphere. This procedure introduces ~0.02 wt% argon into the high pressure conductivity cell from argon gas present in the void space (20 to 30% of the cell volume) between the solid salt particles in the cell. This entrapped argon probably dissolves in the salt when it is melted in the high pressure cell. The dissolution of 0.3 atm of Ar is not expected to change the specific conductance of these molten salts to a measurable extent. This is by analogy with the relatively small effect which dissolved Ar has on the specific conductance of molten NaNO$_3$ as found by Copeland and Zybko.[14]

B. *Apparatus and Procedure.* The electrical conductivity studies on the bismuth trihalides at elevated pressures and temperatures were carried out in a piston-cylinder high pressure chamber similar to the apparatus of Coes,[15] Hall,[16] and Kennedy, *et al.*[17] A conductivity cell (shown schematically in Figure 1) made of fused quartz or of boron nitride with either tungsten, platinum or graphite electrodes was designed to fit within a graphite sleeve furnace, all contained within the high pressure chamber. A metallic-sheathed, MgO-insulated thermocouple junction is located within a well in the upper electrode. This junction is at most 0.5 mm
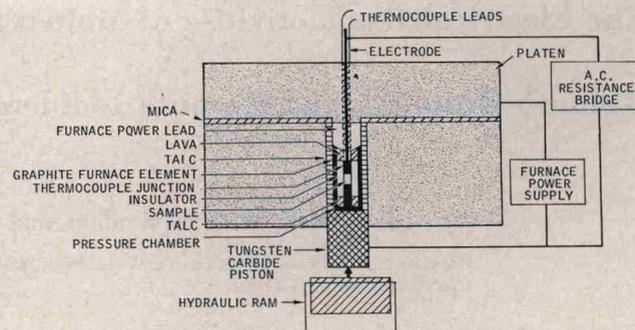
Figure 1. Schematic drawing of high-pressure, high-temperature conductivity cell.

from the molten salt–electrode interface. The conductance cell is approximately 1 mm in diameter and from 7 to 10 mm long. This cell is positioned in the central, most isothermal portion of a graphite sleeve furnace. This furnace is approximately four times the length of the conductivity cell. The method used for determining the pressure and temperature within the high pressure chamber has been described previously.[13]

Electrical conductivity measurements were made with a General Radio Type 1650-A impedance bridge. To check the accuracy of the conductivity bridge under conditions similar to the fused salt impedance measurements, calibrated resistors were substituted for the cell within the pressure chamber at ambient pressure. Thus, all the circuit components external to the cell were equivalent. Lead resistance corrections were also made in these calibration tests. These substituted resistors ranged from 10 ohms to 10^4 ohms, which is greater than the range of resistances encountered in the fused salt measurements (~30–300 ohms). Within these limits, the resistance measured by the impedance bridge agreed to ±2% of the value of the calibrated resistors.

The conductivity data reported for the salts BiCl$_3$, BiBr$_3$, and BiI$_3$ were measured at a frequency of 1000 Hz. However, the effect of frequency on the conductivity of molten BiI$_3$ was measured at a pressure of 5.4 kbars at a temperature of 580° in a quartz cell employing graphite electrodes. These conductivity measurements upon molten BiI$_3$ were made over the frequency range 500–10,000 Hz with a General Radio Type 1311-A audio oscillator and a Type 1232-A tuned amplifier and null detector in conjunction with the Model 1650-A impedance bridge. The conductivity of molten BiI$_3$ at infinite frequency (from an extrapolation

(13) A. J. Darnell and W. A. McCollum, *J. Phys. Chem.*, **72**, 1327 (1968).

(14) J. L. Copeland and W. C. Zybko, *ibid.*, **70**, 181 (1966).

(15) L. Coes, *J. Amer. Ceram. Soc.*, **38**, 298 (1955).

(16) H. T. Hall, *Rev. Sci. Instrum.*, **29**, 267 (1958).

(17) G. C. Kennedy and P. N. LaMori in "Progress in Very High Pressure Research," F. P. Bundy, W. R. Hibbard, and H. M. Strong, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p 30.

of the linear relationship found between $\varkappa$ vs. frequency$^{-1/2}$) differed by less than 2% from the conductivity measured at 1000 Hz. No correction was made for this relatively small frequency dependence of $\varkappa$.

Tests made with boron nitride and quartz blanks showed that the conductivity contribution from the shunt path of the high pressure conductivity cell and its input leads was no greater than 1.5% of the conductance of the molten salt at all temperatures and pressures considered in these measurements. This shunt resistance does, however, become significant at higher temperatures than employed here, i.e., 1000°. Brown and Porter[18] have found that fused fluorides penetrate boron nitride at elevated temperature (i.e., 1000°). Visual inspection and X-ray photography of cross sections of our boron nitride cells indicated no detectable penetration of the boron nitride by the fused bismuth trihalides occurred during a run. Furthermore, results with boron nitride and with quartz cells were essentially the same which also suggests that salt penetration did not take place in the BN cells. Irreversible changes in cell resistance were observed in other runs to higher temperatures (i.e., 1000–1100°) than considered here. It is not known, however, whether this irreversible resistance change was due to salt decomposition or to salt–electrode and/or salt–cell interaction.

The two-probe rather than the usual four-probe method was used in these conductivity measurements. Lead resistance corrections for this two-probe method were obtained from *in situ* measurements with tungsten and nickel blanks substituted in place of the salt sample. Data for these lead resistance corrections as a function of temperature applicable at a pressure of 5.4 kbars are given in Figure 2. This correction consists primarily of the resistance of the leads into the high pressure chamber. These leads, of necessity, must be of relatively small diameter. This lead resistance at 25° is 1.8 ohms. From Figure 2 it is seen that the total resistance from the *in situ* test at high pressure with the tungsten or nickel blank is 2.2 ohms. The difference, 0.4 ohms, is attributed to the two electrode–Ni or electrode–W contact resistances. Electrode–fused salt contact resistances of approximately this same value were found by Grantham[19] for identical size tungsten electrodes in contact with molten $BiCl_3$ and $BiBr_3$ at near atmospheric pressure. Grantham[19] found that temperature has little, if any, effect on this contact resistance. We have assumed that this tungsten–fused salt contact resistance remains small (i.e., 0–0.2 ohm) at the elevated pressures considered here. Graphite electrodes were also used with the salts $BiCl_3$ and BiI_3. Here, the same contact resistance correction as was used for tungsten electrodes was employed. The lowest resistance encountered in these fused salt cells is ~30 ohms. An uncertainty of 0.4 ohm arising from uncertainty of two of the electrode–fused salt contact resistances would therefore amount to an uncertainty of
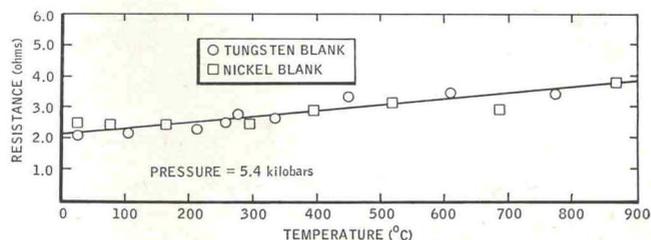
Figure 2. Lead and contact resistance of tungsten and nickel blanks as a function of temperature.

~1% in the resistance of the fused salt cell. However, further measurements would be required in order to establish the effect of pressure on these electrode–fused salt contact resistances.

The cell constant of the high-pressure conductivity cell was determined from its dimensions taken from X-ray profiles after its removal from the high-pressure chamber. Two longitudinal profiles, displaced by 90°, were used to determine the diameter and length of the cell. As a further check, the cell volume was also calculated from the weight of the salt and its density at 25°. The cell volume determined by this procedure and from the dimensions of the cell agreed to within ±5%. The effects which compression (from 1 bar to 5.4 kbars) and thermal expansion (from 25° to the melting point) have upon the cell constant are not known for lack of high-pressure, high-temperature *PVT* data for these salts. These two effects however, compensate for each other to some extent. This cell constant for the solid salt was used to calculate the cell constant of the molten salt at its melting point by assuming the cell dimensions increase proportionally in all directions by an amount determined by the volume of fusion of the salt.[13] Furthermore, the cell constant calculated for the liquid salt at its melting point is used for the entire temperature interval. In the kind of experimental arrangement shown in Figure 1, the amount of salt between the electrodes remains constant both with a variation in pressure and with temperature. It is expected, however, that the conductivity cell dimensions change with a change in temperature and with pressure. If both the diameter and length of the cylindrical conductivity cell change dimensions proportional to the volume change of the molten salt (from thermal expansion and/or compression), then the fractional change in cell constant is approximately equal to the cube root of the fractional volume change due to the change in temperature or pressure. No high-pressure expansivity data are available from which to make these cell constant adjustments. The near atmospheric thermal expansion data of these molten salts[6–8] should, however, give an esti-

(18) E. A. Brown and B. Porter, Bureau of Mines Report R. I. 6500, U. S. Department of the Interior, Washington, D. C., 1963.

(19) L. F. Grantham, private communication.
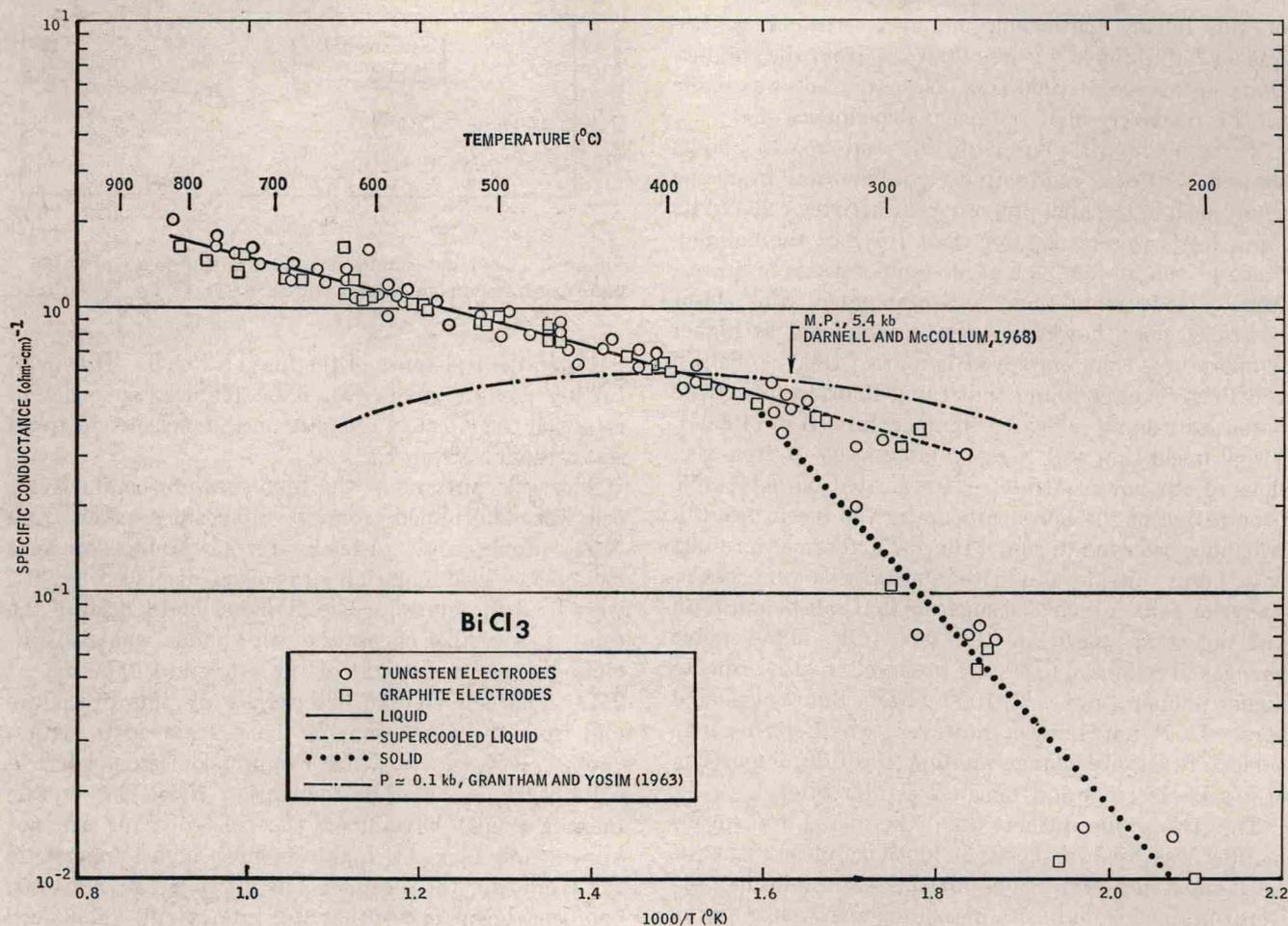
Figure 3. Log κ (ohm-cm)$^{-1}$ vs. $1/T$ (°K) for BiCl$_3$.

mate for the change in cell constant with temperature. For BiCl$_3$ this correction would decrease the specific conductance at most by 15% at 800° since the expansivity at a pressure of 5.4 kbars would be expected to be less than the expansivity at atmospheric pressure. The specific conductivities were calculated using the cell constant obtained for the liquid salt at its melting point.

It is realized this procedure yields cell constants for the liquid salt which are only approximate and that consideration of only the resistance ratios of the salts are necessary for the interpretation of the results given below. However, since the cell conductance is directly proportional to the cell constant, determination of the cell constant gives some measure of the agreement between the isobaric specific conductivities measured on different samples, and on the agreement in the conductivity data between the isobaric and isothermal tests. More significantly, however, specific conductivities give a means of comparison with the conductivity data of Grantham and Yosim[2a] at pressures near atmospheric.

Results

The isobaric specific electrical conductivities of BiCl$_3$, BiBr$_3$, and BiI$_3$ at a pressure of 5.4 kbars are shown in Figures 3–5. The isothermal specific conductivities of these salts at pressures from 3 kbars up to pressures as high as 14 kbars in the case of BiBr$_3$ are shown in Figure 6. The specific electrical conductivity data of Grantham and Yosim,[2] taken at a pressure equal to or somewhat greater than the salts' own vapor pressures (i.e., $P < 0.1$ kbar) are shown for comparison with the isobaric and isothermal data in Figures 3–6.

BiCl$_3$. The specific conductance data for BiCl$_3$ were obtained through use of quartz cells with either tungsten electrodes or graphite electrodes and with a boron nitride cell with tungsten electrodes. The specific conductance obtained with tungsten electrodes is ~10% higher than with the use of graphite electrodes. However, this difference may be due to the uncertainty which arises in the measurement of the cell constant for the two samples. In both cases, conductivity measurements were made from room temperature to 700–800°, then back to room temperature. There appears to be
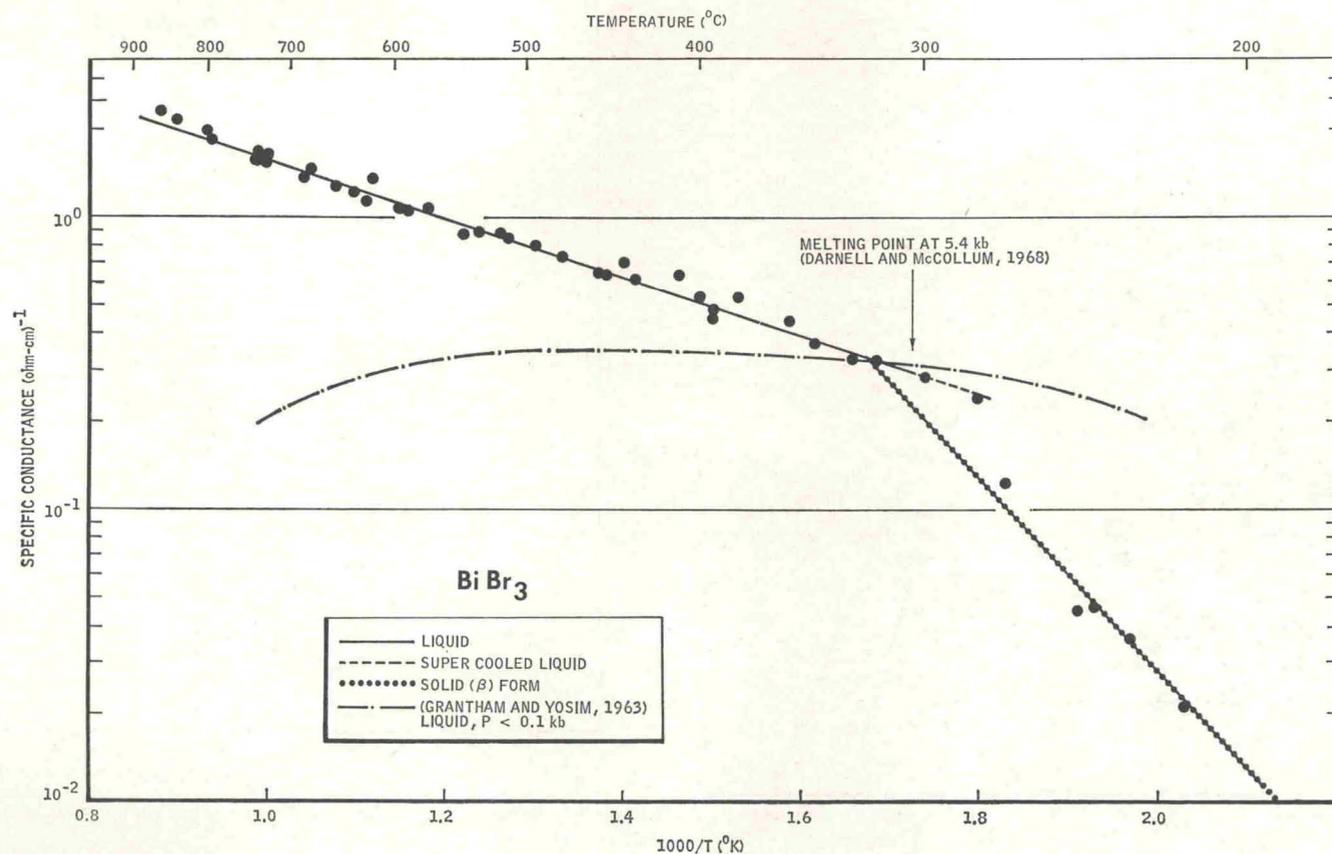
Figure 4. Log $\varkappa$ (ohm-cm)$^{-1}$ vs. $1/T$ (°K) for BiBr$_3$.

no detectable difference in the specific conductance obtained from these consecutive runs. This suggests that neither corrosion nor irreversible deformation occurs in these cells in a given run.

The data for the logarithm of the specific conductance vs. $1/T$ (°K) for both liquid and solid BiCl$_3$, are shown in Figure 3. The intersection of these log $\varkappa$ vs. $1/T$ curves for the solid and the liquid is at 368°. The melting point obtained by differential thermal analysis is 336° at this pressure.[13] The conductivity ratio for the liquid and solid phases at 336° is 1.5. Conductivity measurements for the liquid phase are shown in Figure 3 at temperatures as much as 70° below the melting temperature at this pressure. These measurements for the liquid phase below 336° were obtained on cooling only and are therefore attributed to supercooling of liquid BiCl$_3$. Mayer, et al.,[20] also experienced rather severe supercooling with this salt in their cryoscopic experiments.

The contrast in the behavior of the specific conductance of molten BiCl$_3$ at a pressure of 5.4 kbars (from measurements in this work) and at a pressure of $\sim$0.1 kbar[2a,b] is illustrated in Figure 3. As can be seen from Figure 3, the temperature dependence of the isobaric specific conductance of liquid BiCl$_3$ can, to a first approximation, be represented by the Arrhenius equation

$$\varkappa = A \exp(-E_\varkappa/RT) \qquad (1)$$

The values for the constant A and for the activation energy $E_\varkappa$ were determined empirically by method of least squares from the log $\varkappa$ vs. $1/T$ data for the liquid and solid phases. In this case, the conductivity data obtained from use of tungsten and graphite electrodes were given equal weight. Values obtained for A and

Table I: Constants in the Arrhenius Equation, $\varkappa$ (ohm-cm)$^{-1}$ $= Ae^{-E_\varkappa/RT}$, for the Salts BiCl$_3$, BiBr$_3$, and BiI$_3$ at a Pressure of 5.4 kbars

Salt	A, (ohm-cm)$^{-1}$	$E_\varkappa$, kcal/mol	T, °C
BiCl$_3$,			
solid	6.67×10^4	15.0 ± 2.2	212–336
liquid	9.51	3.68 ± 0.09	273–830[a]
BiBr$_3$,			
β form	9.97×10^4	15.1 ± 1.5	206–315
liquid	16.2	4.62 ± 0.08	282–864[a]
BiI$_3$,			
β form	6.85×10^{10}	42.5 ± 4.3	468–502
liquid	. . .	11	502–886

[a] Includes supercooled liquid.

(20) S. W. Mayer, S. J. Yosim, and L. E. Topol, J. Phys. Chem., 64, 238 (1960).

Figure 5. Log $\varkappa$ (ohm-cm)$^{-1}$ vs. $1/T$ (°K) for BiI$_3$.

Figure 6. Isothermal specific conductance ($\varkappa$) of liquid BiCl$_3$, BiBr$_3$, and BiI$_3$ as a function of pressure.

$E_\varkappa$ are shown in Table I. The activation energies for solid and liquid BiCl$_3$ are 15.0 ± 2.2 and 3.68 ± 0.09 kcal/mol respectively.

Isothermal conductivity measurements at 568° were made on liquid BiCl$_3$ at pressures from 13.5 to 4 kbars. These conductivity data are shown in Figure 6. The specific conductance at 568° is 0.83 (ohm-cm)$^{-1}$ at a pressure of 5.4 kbars. This specific conductance is lower than was obtained from the isobaric experiment at this same pressure and temperature, [1.04 (ohm-cm)$^{-1}$]. These isothermal specific conductance data taken at a temperature of 568° were extrapolated to P = 0 in order to make a comparison with the specific conductance at low pressure. [2] The extrapolated value of $\varkappa$ at P = 0 is 0.38 (ohm-cm)$^{-1}$; the measured value[2a,b] at this temperature and pressure is 0.50 (ohm-cm)$^{-1}$.

BiBr$_3$. The specific conductance of BiBr$_3$ was measured at a pressure of 5.4 kbars using a boron nitride cell with tungsten electrodes. The isobaric (5.4 kbars) specific conductance data for BiBr$_3$ are shown in Figure 4. The low pressure conductivity data of Grantham et al.,[2a] are shown for comparison. Log $\varkappa$ vs. $1/T$ for liquid BiBr$_3$ is linear at a pressure of 5.4 kbars. These log $\varkappa$ vs. $1/T$ data for the liquid and β-BiBr$_3$ phases were each treated by method of least squares in order to evaluate the constants A and $E_\varkappa$ in eq 1. The activa-

tion energies for β-BiBr$_3$ and liquid BiBr$_3$ are 15.1 ± 1.5 and 4.62 ± 0.08 kcal/mol, respectively (Table I). The curves for the solid and liquid intersect at 322°. The melting point obtained at this pressure from differential thermal analysis is 315°.[13] The conductivity ratio of the liquid and solid at 315° is 1.33. Data for supercooled liquid BiBr$_3$ are also shown in Figure 4, but the extent of supercooling is not as great as was found in BiCl$_3$.

Isothermal conductivity measurements were made on BiBr$_3$ over the pressure interval 3.6–14 kbars at a temperature of 623°. These data are shown in Figure 6. In the case of BiCl$_3$ described above, conductivity measurements were made only on the decompression step. However, it was found that if the pressurization cycle was first carried out on the solid salt it could then be carried out on the molten salt. This preliminary pressurization upon the solid salt probably results in a better seal between the electrode and the boron nitride container. As can be seen in Figure 6, hysteresis was observed in the conductivities taken on the compression and decompression cycles. This hysteresis is due to a difference between the actual and indicated pressures on both the compression and decompression procedures. A similar hysteresis effect is also observed in volume vs. pressure curves taken with this same type of piston-cylinder apparatus.[13,17] An averaged $\varkappa$ vs. P curve has been drawn from the separate $\varkappa$ vs. P curves

from the compression and decompression cycles. The specific conductance from the isobaric (5.4 kbars) measurement was 1.20 (ohm-cm)$^{-1}$. The mean value for the specific conductance at a pressure of 5.4 kbars from this isothermal experiment at 623° is considerably lower, being only 0.50 (ohm-cm)$^{-1}$. Extrapolation of this curve for the mean value of the isothermal conductivity to $P = 0$ gives $\varkappa = 0.30$ (ohm-cm)$^{-1}$. Grantham and Yosim[2a] give 0.28 (ohm-cm)$^{-1}$ for the specific conductance of BiBr$_3$ at this temperature and pressure.

BiI$_3$. The specific conductance of BiI$_3$ was measured at a pressure of 5.4 kbars using quartz cells with either tungsten or graphite electrodes or with a boron nitride cell with tungsten electrodes. The specific conductance found with use of tungsten electrodes is almost twice the value obtained with the use of graphite electrodes (Figure 5). This difference in specific conductance of BiI$_3$ from the use of tungsten and of graphite electrodes is much greater than was found in the case of BiCl$_3$. This difference in $\varkappa$ may be due to a reaction between the salt and one of the types of electrodes. On the other hand, it could be due to an initial impurity in one of the samples; probably the one which has the higher conductivity. The temperature coefficient of $\varkappa$ for the liquid phase is, however, approximately the same in both cases. When graphite electrodes were used, the specific conductance from the isobaric experiments agreed with the specific conductance from the isothermal experiments [*i.e.,* at 620° and 5.4 kbars the specific conductance from the isobaric and isothermal experiments are 0.45 and 0.41 (ohm-cm)$^{-1}$, respectively]. Both sets of data are shown in Figure 5; however, only the data from the cell with graphite electrodes were used to obtain the activation energy $E_\varkappa$ reported in Table I. The log $\varkappa$ *vs.* $1/T$ curves for molten BiCl$_3$ and BiBr$_3$ were approximately linear at a pressure of 5.4 kbars. This curve for liquid BiI$_3$ on the other hand shows a curvature with a steeper slope (and thus higher $E_\varkappa$) at higher temperatures. Since $E_\varkappa$ changes with temperature, its value was determined from the slope of log $\varkappa$ *vs.* $1/T$ at the median temperature (690°) of the measurements on the liquid. $E_\varkappa$ for the liquid phase is 11 kcal/mol. From a least-squares treatment the activation energy $E_\varkappa$ for the β phase at a pressure of 5.4 kbars is 42.5 ± 4.3 kcal/mol.

BiI$_3$ has a larger discontinuity in its log $\varkappa$ *vs.* $1/T$ curve at its melting point than does BiCl$_3$ and BiBr$_3$. The ratio of conductivities for the liquid and solid phases is ~3.0. This larger discontinuity in the log $\varkappa$ *vs.* $1/T$ curves and the pressure gradient normally found along the axis of the high pressure conductivity cell[21] probably accounts for the difference in the melting point indicated by these conductivity measurements and the differential thermal analysis results.[13] Little, if any, supercooling occurs in BiI$_3$ since the conductivity *vs.* temperature data upon melting and freezing are very

nearly identical.[13] This was not the case in BiCl$_3$ and BiBr$_3$ where supercooling is extensive.

Isothermal conductivity measurements were made at 620° over the pressure interval 2.5 to 12.6 kbars (Figure 6). These conductivity measurements on liquid BiI$_3$ were limited to pressures below 13 kbars since BiI$_3$ solidifies at this pressure at 620°.[13] As with BiBr$_3$ discussed above, hysteresis was also experienced in the $\varkappa$ *vs.* P curves (taken from the compression and decompression cycles). An average $\varkappa$ *vs.* P curve was constructed from these separate $\varkappa$ *vs.* P curves. Extrapolation of this averaged curve to $P = 0$ yields a specific conductance [0.30 (ohm-cm)$^{-1}$] which is in good agreement with $\varkappa$ measured at low pressures [0.30 (ohm-cm)$^{-1}$].[2a]

Discussion

The molten salts BiCl$_3$, BiBr$_3$, and BiI$_3$ show an exponential increase in specific conductance with decreasing $1/T$ at a pressure of 5.4 kbars. This "normal" or positive temperature coefficient of conductivity at this elevated pressure is in contrast to the behavior of the conductivity as a function of temperature at pressures approximately equal to the salts, own vapor pressures[2a,b] *i.e.,* $P < 0.1$ kbar. At such relatively low pressures, the specific conductivity of these salts was found to exhibit a maximum at a temperature ~150° above the melting point.[2a,b] A maximum in the electrical conductivity *vs.* temperature of the liquid phase has also been found for several other salts.[3-5] Usually an increase in temperature increases the ionic conductivity of a molten salt. This increased conductivity is attributed to an increase in fluidity and thus an increase in the mobility of the ions with increased temperature. Grantham and Yosim[5] suggest that the negative temperature coefficient which they find at extremely high temperatures in several of the salts examined is due to increased covalency or more probably ionic association at high temperature. There are several indications that this increase in covalency results in a decrease in density of the molten salt.[10,11] If the specific volume of the liquid salt increases at high temperatures due to increased ionic association, for example, by a process such as

$$x\text{M}^+ + y\text{A}^- \rightleftharpoons \text{M}_x\text{A}_y \qquad (2)$$

because the molar volume of the associated species is greater than the sum of the molar volumes of the ions from which it is formed, *i.e.,*

$$V_{\text{M}_x\text{A}_y} > xV_{\text{M}^+} + yV_{\text{A}^-}, \qquad (3)$$

then application of an external pressure should, from the principle of Le Chatelier, suppress the association reaction 2.[12] In the absence of other factors, iso-

(21) M. Tamayama and H. Eyring, *Rev. Sci. Instrum.*, **38**, 1009 (1967).

thermal compression would then be expected to increase the specific conductance of partially associated salts due to an increased ionic dissociation. On the other hand, in salts which are highly ionized at ordinary pressures, isothermal compression would not be expected to increase the number of ionic species. High pressure would, however, be expected to increase the viscosity[22] and thus to decrease the mobility of the ions.

Both the dissociation effect and the increased viscosity effect appear to be demonstrated in the bismuth trihalides when the high pressure, isobaric, specific conductance data obtained in this work are compared with the low pressure specific conductance data of Grantham and Yosim.[2a,b] To illustrate, in Figures 3–5 the log $\varkappa$ vs. $1/T$ curves for $P = 5.4$ kbars and $P \leq 0.1$ kbar intersect at temperatures T_i of 390, 322, and 560° for BiCl$_3$, BiBr$_3$, and BiI$_3$ respectively. Thus at temperature T_i, the specific conductivity of the liquid salt is the same at these two pressures, i.e., $\varkappa_{P=5.4\ \text{kbars}} = \varkappa_{P \leq 0.1\ \text{kbar}}$. At temperatures below T_i, the specific conductance $\varkappa$ at $P = 5.4$ kbars is less than $\varkappa$ at $P \leq 0.1$ kbar; here the effect of pressure is to decrease the specific conductance of the molten salt, at least up to a pressure of 5.4 kbars. This decrease in $\varkappa$ is probably due to an increase in viscosity and thus a decrease in mobility of the ions. At temperatures greater than T_i pressure would still be expected to raise the viscosity and therefore lower the conductivity. However, from Figures 3–5 it can be seen that $\varkappa_{P=5.4\ \text{kbars}} > \varkappa_{P \leq 0.1\ \text{kbar}}$ when $T > T_i$. Thus the effect which pressure has upon dissociation is in all likelihood the predominant factor at temperatures greater than T_i. The ratio (α), $\varkappa_{P=5.4\ \text{kbars}}/\varkappa_{P \leq 0.1\ \text{kbar}}$ becomes larger at higher temperatures. This is probably due to a greater degree of ionic association at the lower pressure.

In Table II the conductivity ratio at $P = 5.4$ and $P \leq 0.1$ kbar is compared at (a) the normal melting point,[23] (b) at the temperature of maximum conductance when the salt is under its own vapor pressure,[2a,b] and (c) at the critical temperature of the salt. In the last case,

conductivity data at $P \leq 0.1$ kbar are available only for BiCl$_3$.[2b] The effect of pressure on the conductivity at the critical temperature is large; for BiCl$_3$, $\alpha = 480$.

The isothermal conductivity experiments were, for all the salts considered here, carried out at temperatures greater than T_i. As a further check, it would be useful to examine the pressure dependence of the specific conductance $(\partial \varkappa / \partial P)_T$ of the liquid phase at temperatures below T_i. These measurements were not carried out since the apparatus used here is not suitable for the rather limited and low pressure range required at these low temperatures.

The effect of pressure on $(\partial \varkappa / \partial P)_{T=568°}$ for BiCl$_3$ decreases with increasing pressure and is approaching zero at $P = 13.5$ kbars. This result could be due to almost complete dissociation of BiCl$_3$ at this high pressure. However, it is possible that the viscosity effect may become predominant at these high pressures. If this were the case, then a maximum in the $\varkappa$ vs. P curve might be expected at still higher pressures (BiCl$_3$ solidifies at 24 kbars at this temperature). In the case of BiBr$_3$, the coefficient $(\partial \varkappa / \partial P)_{T=623°}$ is diminishing but still greater than zero at the highest pressure attained (14 kbar). Bismuth tribromide solidifies at a pressure of 29 kbar at this temperature. The pressure coefficient $(\partial \varkappa / \partial P)_{T=620°}$ for BiI$_3$, on the other hand, increases with increasing pressure. Thus both coefficients $(\partial \varkappa / \partial P)_{T=620°}$ and $(\partial \varkappa / \partial T)_{P=5.4\ \text{kbars}}$ for BiI$_3$, unlike those for BiBr$_3$ and BiCl$_3$, increase with increasing pressure and temperature.

The difference in behavior of the specific conductance of molten BiI$_3$ from BiBr$_3$ and BiCl$_3$ at high pressure may be due to the effect of pressure on the stability of these molten salts. For example, there is an increase in volume in the formation of BiI$_3$ (l) from its elements at $P = 1$ atm, i.e., $V_{\text{BiI}_3(l)}$ at its melting point is 127 cm^3/mol;[3] $V_{\text{Bi}(l)} + 3/2 V_{\text{I}_2(l)}$ is only 111 cm^3/mol. Thus liquid BiI$_3$ should become less stable with respect to its elements with an increase in pressure. The molar vol-

Table II: The Specific Conductance Ratio [$\alpha \equiv \varkappa_{P=5.4\ \text{kbars}}/\varkappa_{P=0.1\ \text{kbar}}$] for Molten BiCl$_3$, BiBr$_3$, and BiI$_3$ at Several Temperatures[a]

Salt	α at the normal melting point (hypothetical)[b]		α at temp of max. conductance when $P \simeq 0.1$ kb		α at T_{critical}	
	t, °C	α	t, °C	α	t, °C	α
BiCl$_3$	232	0.75	425	1.15	905	480
BiBr$_3$	218	0.96	425	1.69	...	...
BiI$_3$	408	0.36	525	0.81	...	...

[a] Data for specific conductance at $P = 0.1$ kbar from Grantham and Yosim.[2a,b] [b] Conductivity curve for liquid phase at pressure of 5.4 kbars was extrapolated to a temperature corresponding to the melting point at atmospheric pressure.

Table III: Arrhenius Activation Energy for Conduction in Liquid BiCl$_3$, BiBr$_3$, and BiI$_3$ at 5.4 kbars and at Pressure Equal to or Less than 0.1 kbar

Salt	$E_\varkappa$ at $P = 5.4$ kbars, kcal/mol	$E_\varkappa$[a] at $P \leq 0.1$ kbar, kcal/mol
BiCl$_3$	3.68	3.6
BiBr$_3$	4.62	4.2
BiI$_3$	11	3

[a] Calculated from data in ref 1. $E_\varkappa$ at $P \leq 0.1$ determined from the slope of log $\varkappa$ vs. $1/T$ at temperatures immediately above the melting point.

(22) Reference 12, p 81.

(23) For purposes of comparison, the log $\varkappa$ vs. $1/T$ curve for the liquid at a pressure of 5.4 kbars has been extrapolated to the temperature of the normal or atmospheric melting point.

umes of $BiBr_3$ (l)[7] and $BiCl_3$ (l)[6] are, significantly smaller than the sum of the molar volumes of their respective elements from which they are formed. On this basis, BiI_3 (l) would show a tendency to disproportionate at high pressures whereas $BiBr_3$(l) and $BiCl_3$(l) become more stable. This difference in stability with pressure could account for the difference in behavior of the log $\varkappa$ vs $1/T$ and $\varkappa$ vs. P curves of BiI_3 from those of $BiBr_3$. and $BiCl_3$.

The activation energies ($E_\varkappa$) for $BiCl_3$, $BiBr_3$, and BiI_3 at $P \leq 0.1$ kbar were estimated from the slope of the log $\varkappa$ vs. $1/T$ curves for these salts from data given by Grantham and Yosim[2a] at temperatures immediately above the melting point. These estimated values of $E_\varkappa$ at $P \leq 0.1$ kbar are compared with $E_\varkappa$ at $P = 5.4$ kbars in Table III. The activation energies at these two pressures are essentially identical in the cases of $BiCl_3$ and $BiBr_3$; for BiI_3, $E_\varkappa$ at 5.4 kbars is almost four times its value at $P = 0$. This difference in $E_\varkappa$ between bismuth triiodide and the tribromide and trichloride may be due to a greater effect of pressure upon ionic association in the case of BiI_3.