

from the compression and decompression cycles. The specific conductance from the isobaric (5.4 kbars) measurement was $1.20 \text{ (ohm-cm)}^{-1}$. 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 $0.50 \text{ (ohm-cm)}^{-1}$. Extrapolation of this curve for the mean value of the isothermal conductivity to $P = 0$ gives $\kappa = 0.30 \text{ (ohm-cm)}^{-1}$. Grantham and Yosim^{2a} give $0.28 \text{ (ohm-cm)}^{-1}$ 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 κ 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 κ 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 $0.41 \text{ (ohm-cm)}^{-1}$, 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_κ reported in Table I. The $\log \kappa$ 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_κ) at higher temperatures. Since E_κ changes with temperature, its value was determined from the slope of $\log \kappa$ vs. $1/T$ at the median temperature (690°) of the measurements on the liquid. E_κ for the liquid phase is 11 kcal/mol. From a least-squares treatment the activation energy E_κ 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 $\log \kappa$ 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 $\log \kappa$ vs. $1/T$ curves and the pressure gradient normally found along the axis of the high pressure conductivity cell²¹ 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 κ vs. P curves (taken from the compression and decompression cycles). An average κ vs. P curve was constructed from these separate κ vs. P curves. Extrapolation of this averaged curve to $P = 0$ yields a specific conductance [$0.30 \text{ (ohm-cm)}^{-1}$] which is in good agreement with κ measured at low pressures [$0.30 \text{ (ohm-cm)}^{-1}$].^{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 $\sim 150^\circ$ 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 Yosim⁵ 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



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.*,

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

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 viscosity²² 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 $\log \kappa$ 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.*, $\kappa_{P=5.4 \text{ kbars}} = \kappa_{P \leq 0.1 \text{ kbar}}$. At temperatures below T_i , the specific conductance κ at $P = 5.4$ kbars is less than κ 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 κ 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 $\kappa_{P=5.4 \text{ kbars}} > \kappa_{P \leq 0.1 \text{ kbar}}$ 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), $\kappa_{P=5.4 \text{ kbars}}/\kappa_{P \leq 0.1 \text{ kbar}}$ 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,

Table II: The Specific Conductance Ratio [$\alpha \equiv \kappa_{P=5.4 \text{ kbars}}/\kappa_{P=0.1 \text{ kbar}}$] 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 $P \approx 0.1$ kb | | α at T_{critical} | |
|-----------------|--|----------|--|----------|-----------------------------------|----------|
| | $t, ^\circ\text{C}$ | α | $t, ^\circ\text{C}$ | α | $t, ^\circ\text{C}$ | 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.

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 $(\partial\kappa/\partial P)_T$ 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 $(\partial\kappa/\partial P)_{T=568^\circ}$ 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 κ 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 $(\partial\kappa/\partial P)_{T=623^\circ}$ 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 $(\partial\kappa/\partial P)_{T=620^\circ}$ for BiI_3 , on the other hand, increases with increasing pressure. Thus both coefficients $(\partial\kappa/\partial P)_{T=620^\circ}$ and $(\partial\kappa/\partial T)_{P=5.4 \text{ kbars}}$ 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 $V_{\text{Bi}(l)} + 3/2V_{\text{I}_2(l)}$ 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 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_x | E_x^a |
|-----------------|------------------------------|--------------------------------|
| | at $P = 5.4$ kbars, kcal/mol | 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_x at $P \leq 0.1$ determined from the slope of $\log \kappa$ vs. $1/T$ at temperatures immediately above the melting point.

(22) Reference 12, p 81.

(23) For purposes of comparison, the $\log \kappa$ 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.