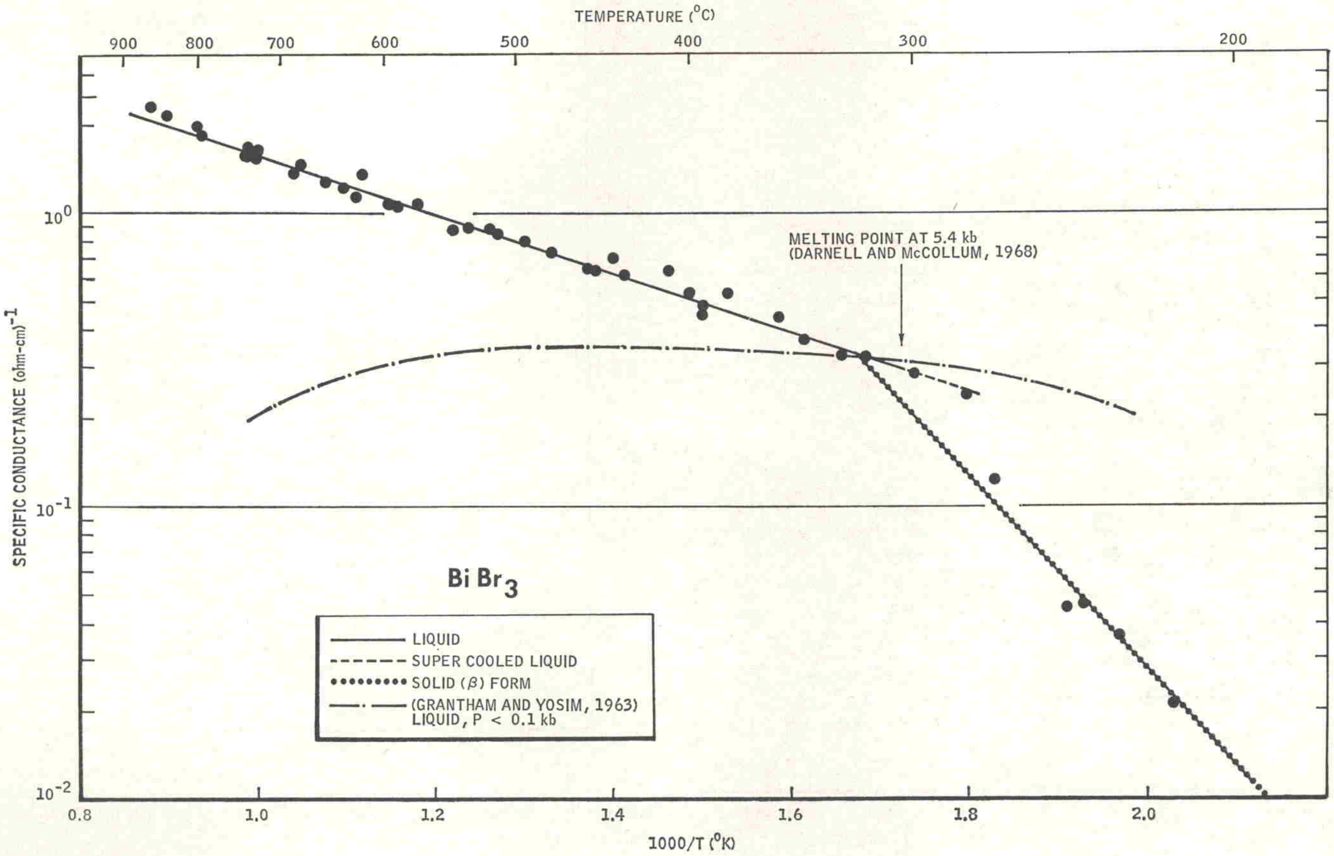

Figure 4. Log $\varkappa$ (ohm-cm)$^{-1}$ *vs.* $1/T$ (°K) for $BiBr_3$.

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 ~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

$$\varkappa = A \exp(-E_\varkappa/RT) \tag{1}$$

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).

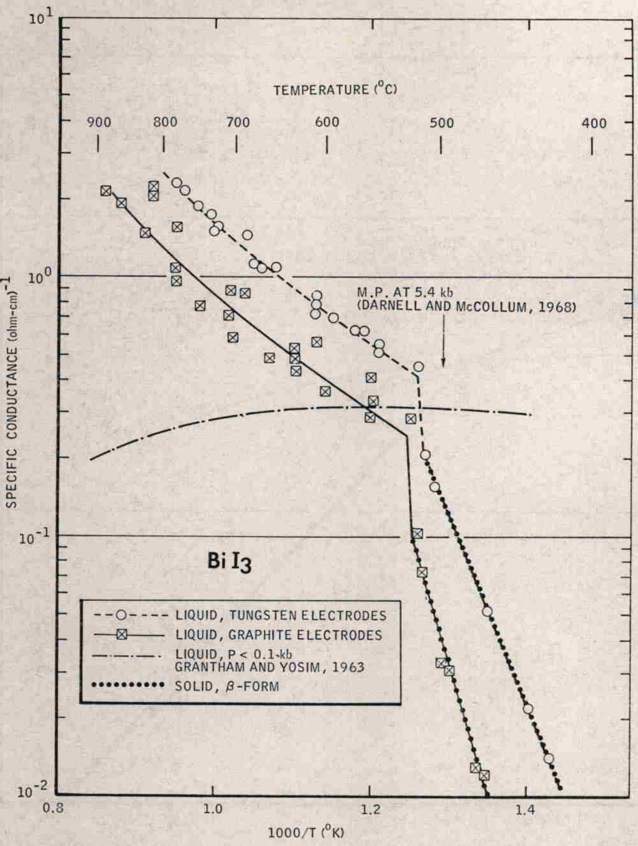

Figure 5. Log $\varkappa$ (ohm-cm)$^{-1}$ *vs.* $1/T$ (°K) for BiI_3.

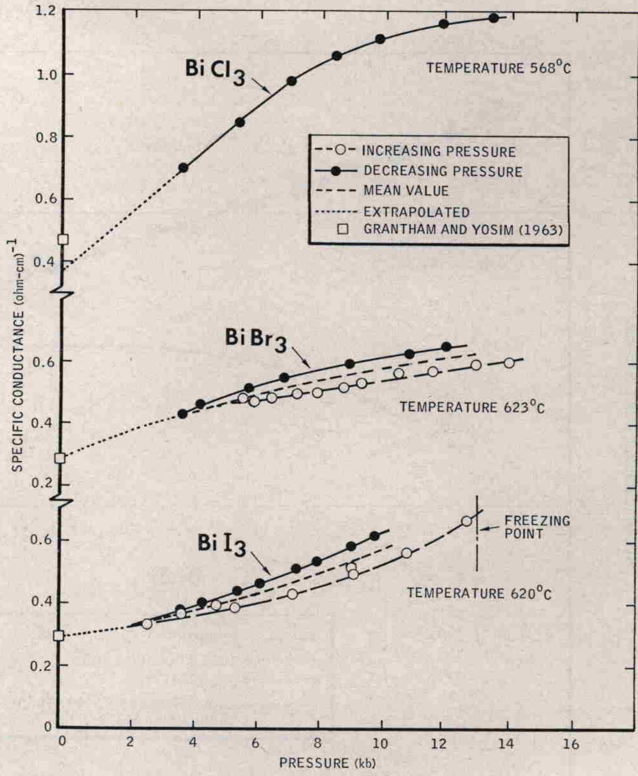

Figure 6. Isothermal specific conductance ($\varkappa$) of liquid $BiCl_3$, $BiBr_3$, and BiI_3 as a function of pressure.

$E_\varkappa$ 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 activation 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