

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

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<sup>18</sup> 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<sup>19</sup> for identical size tungsten electrodes in contact with molten BiCl<sub>3</sub> and BiBr<sub>3</sub> at near atmospheric pressure. Grantham<sup>19</sup> 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<sub>3</sub> and BiI<sub>3</sub>. 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

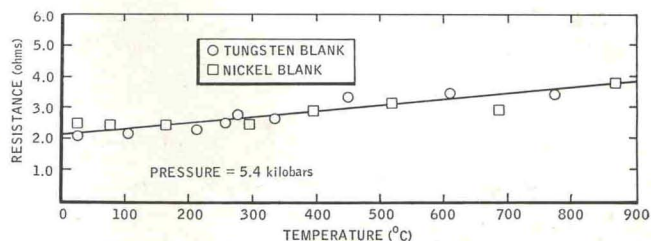


Figure 2. Lead and contact resistance of tungsten and nickel blanks as a function of temperature.

~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.<sup>13</sup> 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<sup>6–8</sup> 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.

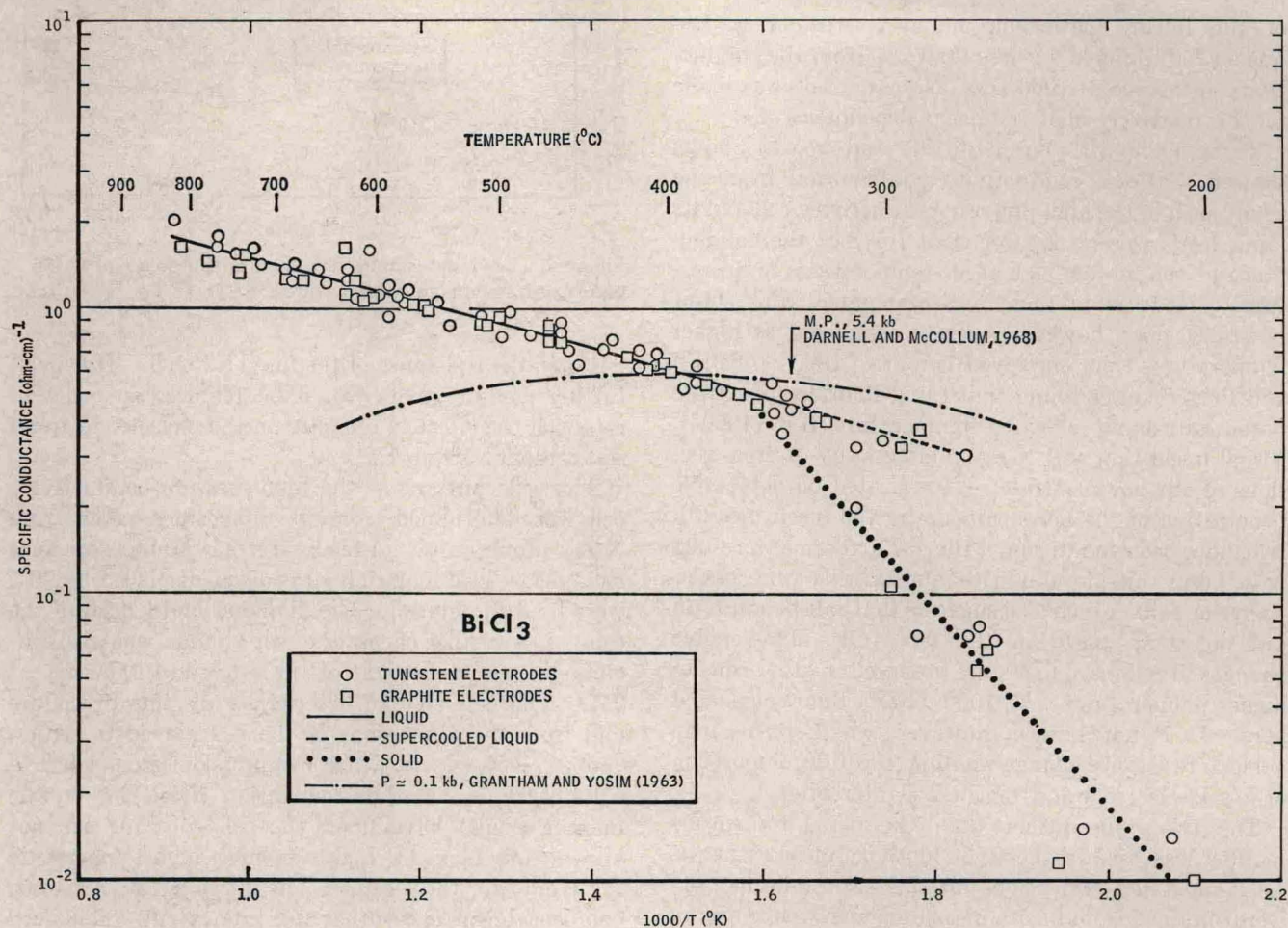


Figure 3.  $\log \kappa$  (ohm-cm)<sup>-1</sup> vs.  $1/T$  (°K) for BiCl<sub>3</sub>.

mate for the change in cell constant with temperature. For BiCl<sub>3</sub> 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<sup>2a</sup> at pressures near atmospheric.

## Results

The isobaric specific electrical conductivities of BiCl<sub>3</sub>, BiBr<sub>3</sub>, and BiI<sub>3</sub> 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<sub>3</sub> are shown in Figure 6. The specific electrical conductivity data of Grantham and Yosim,<sup>2</sup> 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<sub>3</sub>.* The specific conductance data for BiCl<sub>3</sub> 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