

The Electrical Conductivities of Molten Bismuth Chloride, Bismuth Bromide, and Bismuth Iodide at High Pressure¹

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The electrical conductivities of molten BiCl₃, BiBr₃, and BiI₃ were measured at temperatures up to 886° at a pressure of 5.4 kbars. At this elevated pressure the specific conductivity (κ) varies exponentially with $1/T$, *i.e.*, $\kappa \propto e^{-E_{\kappa}/RT}$. 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 κ vs. T curves. The isothermal electrical conductivity of molten BiCl₃, BiBr₃, and BiI₃ was examined at pressures from 3 to 14 kbars. At temperatures above the temperature of maximum conductivity at ordinary pressures, κ 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 BiCl₃,^{2a,b} BiBr₃,^{2a} and BiI₃.^{2a} Negative coefficients have also been found in molten HgI₂,³ InCl₃,⁴ and InBr₃.⁴ This behavior of these salts has been considered anomalous, but other work by Grantham and Yosim⁵ 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 atmospheric⁶⁻⁸ and the compressibility of the solid⁹ 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 association¹² and thus displace or eliminate the negative temperature

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coefficient of electrical conductivity which has been observed in these salts at relatively low pressures.¹² 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

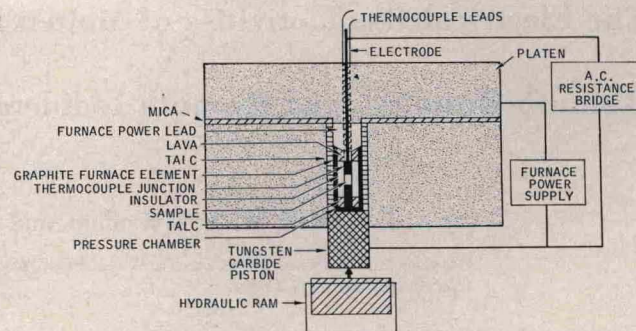


Figure 1. Schematic drawing of high-pressure, high-temperature conductivity cell.

from the molten salt-electrode interface. The conductivity 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 $\pm 2\%$ 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

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