

Effect of Pressure on Electrical Conductivities of Fused Alkali Metal Halides and Silver Halides

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The electrical conductivities of the following fused salts were measured at temperatures up to 860°C and over a pressure range 1-1000 bar: the chlorides, bromides and iodides of the five alkali metals; silver chloride, silver bromide. The volumes $\Delta V_A = -RT(\partial \ln \Lambda / \partial P)_T$ were calculated to be independent of temperature for each salt. ΔV_A was zero for the lithium halides, and increased as the ions were changed in the sequences $\text{Li}^+ \rightarrow \text{Cs}^+$ or $\text{Cl}^- \rightarrow \text{I}^-$. The ΔV_A values were used to find the temperature dependence of conductivity at constant density from that at constant pressure. The results are not consistent with the free volume theory, or with the hole theory of Bockris and Hooper. However, the observed trends are in qualitative accord with the Rice-Allnatt statistical theory of transport in liquids. This theory was used to calculate the conductivity of fused potassium chloride and its pressure and temperature dependence, using ionic pair correlation functions obtained in a computer-simulated ionic dynamics experiment. The results are in moderate agreement with experiment.

We have reported measurements of the pressure dependence of electrical conductivity for fused nitrates and for other salts containing polyatomic anions.^{1, 2} Although the "activation volume", defined by

$$\Delta V_A = -RT(\partial \ln \Lambda / \partial P)_T, \quad (1)$$

varied in a systematic way as the cation and anion sizes were changed, interpretation of the results in terms of ionic interactions was complicated by the non-spherical shape of the anions. More detailed discussion becomes possible if the ions in the melt are spherical; an effective pair potential can then be written in which the internuclear distance is the only variable.³⁻⁶ The fused alkali halides satisfy this requirement; they are the simplest of ionic liquids, occupying a position in relation to fused salts similar to that of the liquid rare gases in the field of molecular fluids.

We report measurements of the isothermal pressure dependence of conductivity for the fused alkali metal chlorides, bromides and iodides, and silver chloride and bromide. An externally heated pressure vessel was used, and the pressure-transmitting fluid was argon. This arrangement allowed stable pressure and temperature conditions to be established in the zone containing the conductivity cell. We have derived the temperature dependence of conductivity at constant density from that at constant pressure, using the equation¹

$$(\partial \ln \Lambda / \partial T)_V = (\partial \ln \Lambda / \partial T)_P + (\partial \ln \Lambda / \partial P)_T (\partial P / \partial T)_V. \quad (2)$$

Values of $(\partial P / \partial T)_V$ were either measured directly or were calculated from published values of expansivity α and compressibility β by the expression

$$\left(\frac{\partial P}{\partial T} \right)_V = - \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P / \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{\alpha}{\beta}. \quad (3)$$