Pressure Dependence of Electrical Conductivity for Fused Mercuric Halides

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The electrical conductivities of molten $HgCl_2$, $HgBr_2$ and HgI_2 have been measured over the pressure range 1-1000 bar at temperatures between 260°C and 370°C. In each case the conductivity increased with pressure; at 300°C, the specific conductance " activation volume " $\Delta V_\kappa = -RT(\partial \ln \varkappa/\partial P)_T$, was -50 cm^3 mol^{-1} for $HgCl_2$, -65 cm^3 mol^{-1} for $HgBr_2$ and -102 cm^3 mol^{-1} for HgI_2. These increases in conductivity are attributed to the displacement of ionization equilibria of the type $2HgX_2 \rightleftharpoons HgX^+ + HgX_3^-$ (X = halogen). The Born equation was used to estimate the volume changes associated with ionization, with results in reasonable accord with the experimental values. The pressure required to cause complete ionization is estimated to be in the range 5-10 kbar. For molten HgI_2, d.c. electrolysis experiments showed that the increase in conductivity with pressure was *not* caused by the onset of electronic conductivity. Although the conductivity at constant pressure decreases with temperature for HgI_2, and passes through a maximum with rising temperature for $HgBr_2$ and $HgCl_2$, the conductivity at constant density increases with temperature for all three compounds.

Grantham and Yosim [1] have studied the temperature dependence of electrical conductivity for a wide range of metal halides in equilibrium with their vapours. They found that the conductivity usually increased as the temperature was raised from the melting point, but the rate of increase diminished with rising temperature. In some cases the conductivity-temperature curve passed through a maximum, and for mercuric iodide the conductivity decreased with rising temperature over the whole liquid range. In accounting for these results, Grantham and Yosim suggested that the melts contain covalent molecules in equilibrium with ions, the conductivity being proportional to the product of ion mobility and degree of dissociation. The former increased with rising temperature, causing the increase in conductivity generally observed at lower temperatures. However, the degree of dissociation decreased with temperature, giving rise to the conductivity maximum and subsequent decrease. This fall in the degree of dissociation was thought to be principally a consequence of the density change rather than of the temperature change itself, and the authors suggested that the conductivity would always increase with temperature under conditions of constant density. They recognized that measurements involving pressure as an independent variable would be required to confirm this hypothesis.

We report measurements of the pressure dependence of conductivity for molten $HgCl_2$, $HgBr_2$ and HgI_2, in the range 1-1000 bar and 260-370°C. The conductivity increased with pressure at constant temperature in each case, in contrast to the behaviour of fully ionized salts such as the alkali nitrates.[2] Using compressibilities and expansivities taken from the literature, the isochoric temperature coefficients of conductivity have been calculated, and are indeed found to be positive, in accordance with the suggestion of Grantham and Yosim.

EXPERIMENTAL

MATERIALS

$HgCl_2$ (British Drug Houses Ltd., >99.5 %) was distilled five times in an all-glass apparatus. $HgBr_2$ (B.D.H., 98 %) was distilled three times in all-glass apparatus, sublimed twice in a stream of argon saturated with bromine vapour at 20°C and finally distilled once. HgI_2 (B.D.H., 99 %) was sublimed once in a stream of air. The purified salts were cast into sticks before loading into the conductivity cells.

CONDUCTIVITY MEASUREMENTS ON HgI_2

The conductivity cell illustrated in fig. 1 was made from Pyrex. The cell constant was 209 cm^{-1}, and was determined using 0.01 Demal KCl solution at 25.0°C. The change in cell constant between 25°C and 368°C is about 0.1 %, which is insignificant. The cell constant is not needed for the evaluation of ΔV_κ, and has been used only in comparing our results with those of previous workers. The loaded cell was suspended inside a heated pressure vessel ; pressure was applied by admitting argon. The vessel, conductance bridge and general procedure have been described elsewhere.[2] Access of dissolved argon to the central part of the conductivity cell was prevented by providing a long, narrow diffusion path from the exposed surfaces of the melt. The conductance showed no hysteresis when the pressure was cycled isothermally between atmospheric pressure and 1000 bar over a period of 8 h. Temperatures were measured with a stainless steel sheathed, chromel-alumel thermocouple inside the hot vessel, with its junction positioned near the central capillary of the conductivity cell. The temperature was constant to within ± 0.25°C for all measurements in a given pressure cycle. A pressure of 1 kbar changes the e.m.f. of a chromel-alumel couple by an amount corresponding to about 0.1°C, which is too small to warrant application of a correction.[3]

At the higher temperatures the escape of HgI_2 from the cell by evaporation caused concern, as the vapour corroded the pressure vessel and also condensed in the gas outlet tube, causing blockages. The rate of evaporation was reduced to an acceptable level by placing a 1 cm layer of fused $LiNO_3$ on the free surfaces of HgI_2. $LiNO_3$ and HgI_2 have very similar melting points and form two-phase liquid mixtures with very little mutual solubility.[4] Some measurements made without the $LiNO_3$ gave identical results, showing that diffusion of dissolved $LiNO_3$ into the conduction path was not a significant source of error. Isotherms measured under both conditions are included in fig. 3.
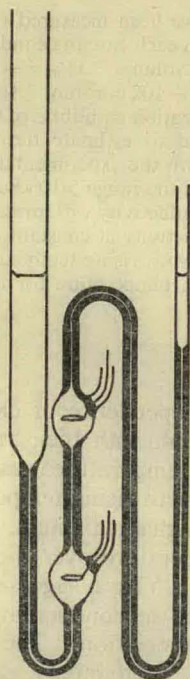
FIG. 1.—Conductivity cell used for HgI_2.

CONDUCTIVITY MEASUREMENTS—$HgBr_2$ AND $HgCl_2$

Attempts to measure the conductivity of these compounds in the above apparatus were abandoned, because corrosion of the inside of the pressure vessel and of the stainless steel thermocouple sheath occurred rapidly at 300°C. A new apparatus was designed, in which these difficulties were avoided (see fig. 2). Use was made of a vertically-mounted pressure vessel provided with a heating mantle at the upper end, and a water jacket at the lower end, above the flange closure. The heater was divided into three parts; by adjusting rheostats in parallel with these the temperature gradient in a 3 cm long section was reduced to 0.25°C or less at temperatures and pressures in the range 300-450°C and 1-1000 bar. The conductivity cell was positioned in this isothermal zone, and was covered by a Pyrex tube which was closed at its upper end and which extended downwards into the cold region. Vapour diffusing