FIG. 4. Isothermal specific conductance (K) of $HgCl_2$ as a function of pressure (kbar).

perature limit to which the Teflon cell can be heated without contamination of $HgCl_2$.) It was then cooled, removed from the high-pressure apparatus (as a further precaution the weight and the dimensions of the cell were checked). The conductivity was again measured at 281°C at pressure of 1 atm. The data from this test are shown in Fig. 3. The conductivities before and after pressurization are seen to be in good agreement. These results as well as the results shown in Fig. 4 demonstrate that this effect of pressure upon the conductivity of molten $HgCl_2$ which we observe is indeed reversible.

The temperature dependence of the isobaric specific conductance of liquid $HgCl_2$ at a pressure of 5.4 kbar can, to a first approximation, be represented by the Arrhenius equation

$$K = A \exp(-E_k/RT). \tag{2}$$

Values for the constant A and of the activation energy for conduction (E_k) were determined empirically by the method of least squares from the $\log K$ vs $1/T$ data. A and E_k are 2.13 ± 0.09 $(\Omega \cdot cm)^{-1}$ and 8.46 ± 0.14 kcal/mole, respectively.

2. HgI_2

The conductivity of molten HgI_2 was measured over the temperature range 292–620°C at a constant pressure of 5.4 kbar. The results from these measurements are shown in Fig. 5. Conductivity measurements were attempted at higher temperatures (i.e., up to 800°C). However, an irreversible change in the conductivity was found to occur at temperatures above 650°C. The electrodes were changed from Pt to W—however, without success. Below 650°C use of both types of electrodes gives essentially identical results (see Fig. 5;

with sample No. 3 Pt electrodes were used; with No. 4 W electrodes were employed). Note that conductivity measurements made from 322 down to 292°C were upon a supercooled liquid phase.

Conductivity data for molten HgI_2 reported by Grantham and Yosim[5] at a pressure approximately equal to the salts own vapor pressure (i.e., $P < 0.1$ kbar) are also shown in Fig. 5 for comparison with these conductivity data taken at a pressure of 5.4 kbar. Here, as in the previous case with $HgCl_2$, an increase in pressure causes an increase in the conductivity of HgI_2 (at a given temperature). However, the ratio for the change in conductivity for a pressure change from 0.1 to 5.4 kbar is considerably less than was found in the case of $HgCl_2$. On the other hand, the conductivity of HgI_2 is some three orders of magnitude greater than K for $HgCl_2$ at the respective melting points of these two salts at atmospheric pressure.[1–4]

An unusual result is noted in the temperature coefficient of conductivity of molten HgI_2 when the pressure of the salt is increased from a pressure equal to its own vapor pressure to a pressure of 5.4 kbar. At ordinary pressure the temperature coefficient of conductivity is negative.[4] At 5.4 kbar the temperature coefficient is positive and the $\log K$ vs $1/T$ (degree Kelvin) plot is linear. As in the previous case with $HgCl_2$, we have subjected these data to a least squares analysis in order to obtain the best linear fit in terms of two constants, A and E_k, The value for A is 0.36 ± 0.04 $(\Omega \cdot cm)^{-1}$; for E_k it is 2.53 ± 0.12 kcal/mole.

The effect of pressure upon the conductivity of molten HgI_2 was also examined at constant temperature over the pressure range 3 to 20 kbar (Fig. 6). These measurements were carried out at a temperature of 555 ± 5°C. It can be seen from Fig. 2 that HgI_2 remains a liquid at this temperature at the highest pressure (20 kbar) used in this test. The same experimental techniques which were employed with $HgCl_2$ were also used here; however, the conductivity cell ruptured in an attempt to repressurize the test cell to 20 kbar. The value for the specific conductivity upon decompression at an indicated pressure of 5.4 kbar is 9×10^{-2} $(\Omega \cdot cm)^{-1}$. This is in fair agreement with the conductivity obtained in the isobaric measurement at this same temperature of 555°C [from Fig. 3, $K = 8 \times 10^{-2}$ $(\Omega \cdot cm)^{-1}$ at this temperature]. The conductivity at 5.4 kbar upon this decompression cycle agrees with the initial value obtained for the conductivity of this same sample made at a pressure of 5.4 kbar before this sample was carried to a pressure of 20 kbar. On this basis it appears that the effect upon the conductivity of molten HgI_2 is reversible over the pressure interval 3 to 20 kbar.

IV. DISCUSSION

The high vapor pressure, low viscosity, and low specific conductance indicate that the molten mercuric halides $HgCl_2$, $HgBr_2$, and HgI_2 are largely molecular or
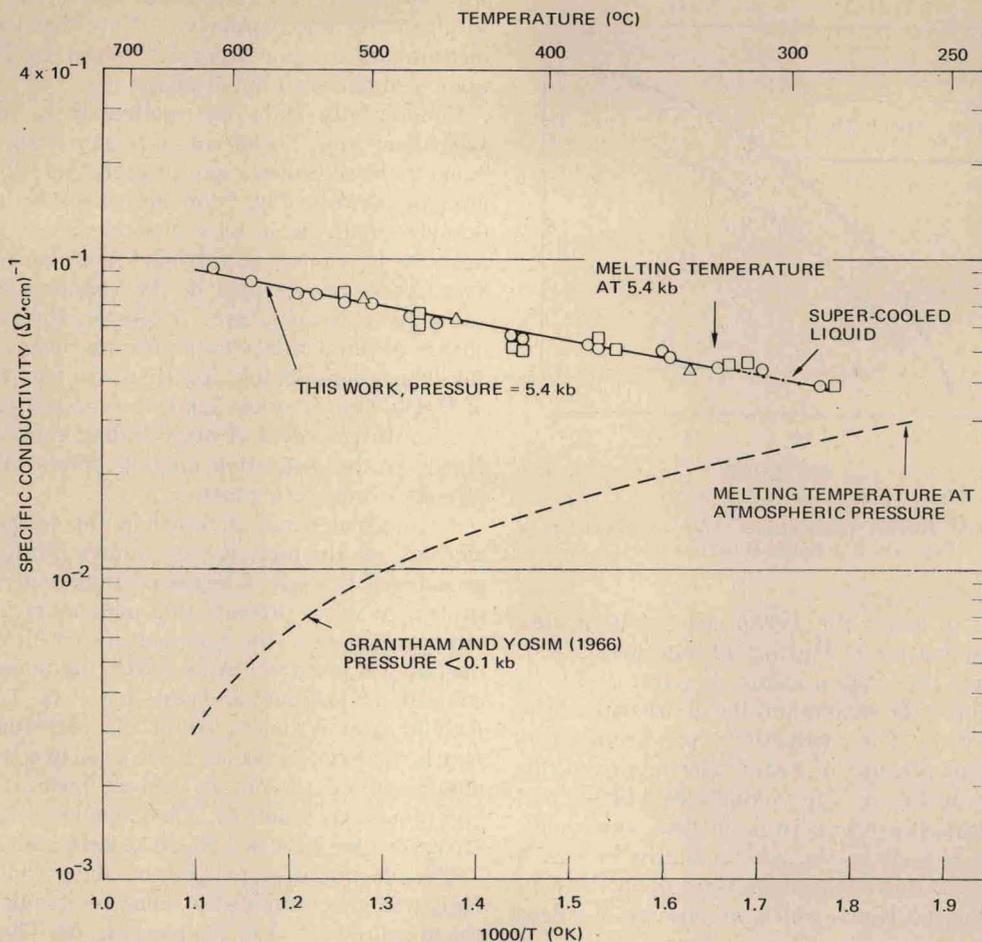
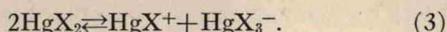FIG. 5. $\text{Log} K (\Omega \cdot \text{cm})^{-1}$ vs $1/T$ (°K) for HgI₂. (○) Sample No. 3, Run No. 3; (□) Sample No. 3, Run No. 4; (△) Sample No. 4, Run No. 1. Pressures given in kbars.

associated at ordinary pressures.[18] Janz and McIntyre[14] have suggested that the species in the molten state of these compounds may involve an equilibrium between molecular and ionic species such as

$$2HgX_2 \rightleftharpoons HgX^+ + HgX_3^-. \qquad (3)$$

The low electrical conductivity of these molten salts indicates that they are only slightly dissociated; the order of decreasing conductance, iodide > bromide > chloride, reflects the relative degree of dissociation.[3]

The temperature coefficient of conductivity of a liquid in which an equilibrium such as (3) is neither far to the left (molecular) nor far to the right (strong electrolyte) might be expected to exhibit a complicated behavior since a change in temperature might also shift this equilibrium and thus the number of the ionic species available for the conduction process in addition to the usual effect of temperature upon the mobility of the conducting species.

Grantham and Yosim have indeed observed a maximum in the temperature coefficient of electrical conductivity of several salts.[5-7] In such a case, this maximum has been observed in the K vs T curve when the electrical conductivity was measured under the conditions where the molten salt was allowed to expand freely as the temperature was increased.[19] (The salt was under a pressure closely approximating its own vapor pressure in these measurements carried out by Grantham and Yosim.[5,7,9]) Yosim[20] has pointed out that it would be advantageous to measure the electrical conductivity of such systems wherein the liquid kept at constant volume. However, neither the experimental apparatus nor the necessary PVT data are currently available with which to carry out such constant volume conductivity measurements over an extended temperature range, i.e., as much as 500°C above the normal melting point. As an alternative, the electrical conductivity of the molten state of these relatively low