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Fusion Curve and Electrical Conductivity of Molten HgCl_2 and HgI_2 at Elevated Pressure*

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The fusion curves of HgCl_2 and HgI_2 were measured to a pressure of 22 kbar. The melting temperature can be represented as a function of pressure by $t_P = t_0 + b_1P + b_2P^2$, where t_P is the melting temperature in degrees Centigrade at a pressure P in kilobars; b_1 and b_2 are constants. Values for t_0 (deg), b_1 (deg kbar⁻¹), and b_2 (deg kbar⁻²) are 276, 259; 19.8, 17.1, and -0.26 , -0.41 , respectively. The electrical conductivities (K) of molten HgCl_2 and HgI_2 were measured to 805 and 620°C, respectively, at a pressure of 5.4 kbar. The electrical conductivity of $\text{HgCl}_2(\text{l})$ was also measured from 557 to 634°C at $P = 20.5$ kbar. At these elevated pressures K varies exponentially with $1/T$, i.e., $K \cong A \exp(-E_k/RT)$. At 5.4 kbar, $A = 2.13$ and 0.36 ($\Omega \cdot \text{cm}$)⁻¹; $E_k = 8.46 \pm 0.14$ and 2.53 ± 0.12 kcal/mole, respectively, for molten HgCl_2 and HgI_2 . The behavior of $\text{HgCl}_2(\text{l})$ and $\text{HgI}_2(\text{l})$ at this elevated pressure is now typical for a strong electrolyte. This is in contrast to their behavior at ordinary pressures where HgCl_2 shows a maximum in its K vs T curve and HgI_2 has a negative temperature coefficient of K from the onset of melting. The conductivities of molten HgCl_2 and HgI_2 were also examined from 3 to 20 kbar at constant T . At 600°K, $K_{P=20 \text{ kbar}}/K_{P=3 \text{ kbar}}$ for $\text{HgCl}_2 = 12.4$; at 555°K this ratio for HgI_2 is 1.66. Thus pressure increases the conductivity of these salts. This is attributed to a greater degree of ionic dissociation at elevated pressures.

I. INTRODUCTION

The electrical conductivities of the molten mercuric halides suggest that they are predominantly covalent in character.¹⁻³ Hevesy⁴ has observed that $\text{HgI}_2(\text{l})$ has a negative temperature coefficient from the onset of melting. Grantham and Yosim⁵ found that molten HgCl_2 and HgBr_2 have a maximum in their specific electrical conductivity vs temperature (K vs T) curves approximately 200° above their melting points. These measurements by Grantham and Yosim were carried out with the salt at its own vapor pressure. Similar conductivity maxima were found by them in other molten salts, i.e., in the bismuth trihalides^{6,7} and in ZnI_2 , CdI_2 , SnCl_2 , and in CuCl .⁵ These authors attribute these maxima in K to increased ionic association at higher temperatures. Darnell, McCollum, and Yosim⁸ have shown that extreme pressure increases the electrical conductivity of BiCl_3 , BiBr_3 , and BiI_3 and furthermore removes this maximum in the K vs T curve.

The pressure-temperature phase diagrams of HgCl_2 and HgI_2 were examined to determine the extent of the liquid phase at pressures up to 22 kbar. The electrical conductivities of molten HgCl_2 and HgI_2 were then measured at elevated pressure, first as a function of temperature at constant but elevated pressure, then as a function of pressure at constant temperature.

II. EXPERIMENTAL

A. Materials

Reagent-grade HgCl_2 and HgI_2 were further purified by distillation under a partial pressure of oxygen⁹ and then sublimed in vacuo. The purified compounds were loaded into the conductivity cells within an inert-atmosphere glove box.

B. Apparatus and Procedure

The phase diagram studies and electrical conductivity measurements on HgCl_2 and HgI_2 were carried out in a piston-cylinder high-pressure apparatus using an internally heated furnace. The apparatus and procedure used here have been described in previous papers by Darnell *et al.*^{8,10} The pressure-temperature phase diagrams of HgCl_2 and HgI_2 were determined using differential thermal analysis (DTA) and resistivity measurements. The solid-liquid curve was examined both upon freezing and melting over the pressure range 2-22 kbar. Platinum and/or nickel cells were used as sample containers in these DTA measurements. In all cases the freezing point of the salt was redetermined at low temperature (and at low pressure) after measurements had been made at higher temperatures. This was done in order to ascertain that the freezing point and

thus the purity had not changed as a result of exposure to higher temperatures.

The conductivity measurements upon molten HgCl_2 and HgI_2 were made following the technique used by Darnell *et al.*⁸ for the bismuth trihalides. For HgCl_2 , a quartz cell with platinum electrodes was used; for HgI_2 both Pt and W electrodes were used. Use of either electrode material yielded essentially the same value for the specific conductivity for HgI_2 .

A checking procedure was also used here in order to ascertain that exposure of these compounds to high temperature and/or high pressure did not irreversibly change the cell constant or cause contamination of the compound. In this procedure the conductivity was first determined at a temperature just above the melting point at a pressure of 5 kbar. The conductivity was then redetermined at this same pressure and temperature after the sample had been exposed to higher temperatures and/or higher pressures. In general we found that temperatures above 850°C and pressures above 25 kbar resulted in significant irreversible changes in the conductivity when remeasured at the low-temperature check point at 5 kbar.

The electrical conductivities reported here were determined at a frequency of 1000 Hz. The conductivity, however, was examined as a function of frequency (500–5000 Hz) at one pressure (5.4 kbar) and temperature (500°C) for HgCl_2 and HgI_2 . No dependency of K upon frequency was noted within the limit of precision of these measurements.

Stainless-steel-clad chromel–alumel junctions were placed within the high-pressure chamber to measure the temperature of the compound. No corrections have been applied to account for the effect of pressure upon the emf of these couples; however, this effect is reported to be small (i.e., less than 1%) at pressures below 20 kbar.¹¹

III. RESULTS

A. Phase Studies

The pressure–temperature phase diagrams for the condensed phases of HgCl_2 and HgI_2 are shown in Figs. 1 and 2, respectively. In each case the solid \rightleftharpoons liquid transition curve was determined to a pressure of 22 kbar. Both melting point and freezing point determinations were made upon these compounds using DTA and resistance measurement techniques. No polymorphic transition was observed in HgCl_2 at pressures up to 45 kbar and at temperatures up to 500°C. The red \rightleftharpoons yellow polymorphic transition in HgI_2 was detected by its resistance change. The results obtained here for this polymorphic transition are compared with Bridgman's¹² data in Fig. 2. Brasch *et al.*¹³ have shown that the polymorphic transition which occurs at a pressure of 13 kbar at room temperature is the same as the red \rightleftharpoons yellow transition which is observed at 127°C at

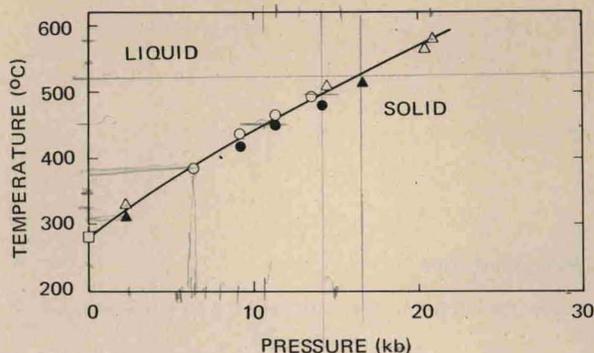


FIG. 1. Pressure–temperature phase diagram of HgCl_2 . (Δ) melting; (\blacktriangle) freezing, by differential thermal analysis. (\circ) melting; (\bullet) freezing, by resistance measurements. (\square) melting point at 1 atm. Pressure in kilobars.

atmospheric pressure. This solid–solid transition is somewhat unusual since a maximum is exhibited in its P – T curve.

Equations for the melting temperature vs pressure for HgCl_2 and HgI_2 were computed by method of least squares of the experimental data and are given in the polynomial form,

$$t_p = t_0 + b_1P + b_2P^2, \quad (1)$$

where t_p is the melting point (degrees centigrade) at pressure P (kilobars), t_0 is the melting temperature at 1 atm, b_1 and b_2 are constants. Values for the constants of this melting curve equation obtained for HgCl_2 and HgI_2 are given in Table I.

The constant b_1 in Eq. (1) gives the initial (atmospheric pressure) slope of the melting curve. For HgCl_2 , b_1 is 19.8 deg/kbar; for HgI_2 it is 17.1 deg/kbar. As a comparison the initial slope of the melting curve was calculated by use of the Clausius–Clapeyron equation, $dT/dP = k\Delta V/\Delta S$, where k is a proportionality constant, ΔV and ΔS are the volume and entropy of fusion. Taking Janz's¹⁴ values of 11.4 cm³/mole for ΔV_f and 7.5 cal/mole deg for ΔS_f of HgCl_2 yields 15.7 deg/kbar for the initial slope of the melting curve for HgCl_2 . Using Topol's¹⁵ entropy of fusion of 8.40 cal/mole/deg gives 17.6 deg/kbar for the slope, dT/dP at atmospheric pressure. Likewise using 14.5 cm³/mole and 8.6 cal/mole/deg for ΔV_f and ΔS_f of HgI_2 ¹⁴ gives 14.2 deg/kbar for the slope of the liquid \rightleftharpoons solid P – T curve at atmospheric pressure. The molar volume of the yellow (high temperature) form of HgI_2 has been used to calculate the volume change during fusion. For both compounds the calculated value of dT/dP from the Clausius–Clapeyron equation is in relatively good agreement with the measured value of the slope of the melting curve, i.e., for HgCl_2 dT/dP (calc) is 15.7 (Janz's ΔS_f) or 17.6 (Topol's ΔS_f) the measured value is 19.8 deg/kbar; for HgI_2 dT/dP (calc) is 14.2, measured 17.1 deg/kbar.