FIG. 2. Pressure-temperature phase diagram of HgI₂. ($\triangle$) melting; ($\blacktriangle$) freezing, Sample No. 4 ($\bigcirc$) melting; ($\bullet$) freezing, Sample No. 5. ($\square$) melting point at 1 atm. ($\triangledown$) red–yellow transition. Pressure in kilobars.

B. Electrical Conductivity

The electrical conductivities of molten $HgCl_2$ and HgI_2 were examined (a) as a function of temperature at a constant but elevated presure and (b) as a function of pressure at constant temperature.

1. $HgCl_2$

The conductivity of molten $HgCl_2$ was measured over the temperature range 327 to 805°C at a pressure of 5.4 kbar. The results are shown in Fig. 3. It should be noted that the melting point at this pressure of 5.4 kbar is 368°C (Fig. 1); thus the conductivity measurements between 327° and 368° were made upon the super-cooled liquid.

The conductivity of $HgCl_2$ was also measured at a pressure of 20.5 kbar from 557°C (the melting temperature at this pressure) to 634°C. Two separate attempts which were made to measure the conductivity to higher temperatures at this pressure resulted in failure of the conductivity cell. The conductivity data over this rather limited temperature range at 20.5 kbar suggest that the slope of $\log K$ vs $1/T$, is not greatly different from the slope obtained at 5.4 kbar.

Conductivity data for molten $HgCl_2$ reported by Grantham and Yosim[5] at a pressure approximately equal to the salts own vapor pressure ($P < 0.1$ kb) are also shown in Fig. 3 for comparison with our data obtained at a much higher (but constant) pressure. Two differences are immediately apparent from comparison of K at 5.4 kbar and at the lower pressure. First of all, it can be seen that an increase in pressure brings about a large increase in the specific conductivity of molten $HgCl_2$. For example, at 600°C the specific conductivity increases by more than three orders of magnitude as the pressure is increased from near atmospheric pressure up to a pressure of 20.5 kbar.

Second, the behavior of the conductivity with temperature variation is markedly altered at these elevated pressures. At temperatures up to $\sim 150°C$ above the melting point the slopes of $\log K$ vs $1/T$ curves for the two widely different pressures (near atmospheric and 5.4 kbar) are similar (Fig. 3). However, at higher temperatures this similarity in slopes no longer exists. Grantham's and Yosim's conductivity data[5] show a maximum at 480°C and consequently exhibit a decrease in specific conductivity with increasing temperature above 480°C.

The effect of pressure upon the conductivity of molten $HgCl_2$ at constant temperature was also examined. The results from measurements carried out at 600° are shown in Fig. 4. Here, the variation in conductivity with pressure over the interval 3 to 20 kbar is shown. (The specific conductivity is only approximate in this case since the compressibility of the molten salt is not known. The cell constant has been adjusted, as an approximation, taking into account the compression experienced by the entire high-pressure chamber assembly.) A temperature of 600° was chosen because here, $HgCl_2$ remains a liquid at all pressures below 20 kbar. The data shown in Fig. 4 were obtained after compressing solid $HgCl_2$ to a pressure of 20 kbar at 25°C and then raising the temperature to 600°C. Conductivity data were then taken as the pressure was decreased from 20 to 3 kbar (upper curve in Fig. 4). Following this, conductivity measurements were made as the pressure was increased to 17.5 kbar. The temperature and pressure were then returned to the original reference condition of 350°C and 5.4 kbar and the conductivity was again remeasured at this pressure and temperature and was found to be almost identical to its original value at this same temperature and pressure. It can be seen in Fig. 4 that hysteresis is exhibited in the K vs P curves for the decompression and compression stages. However, this is to be expected in this kind of experimental procedure[16] where the pressure within the high-pressure chamber is calculated from the force applied to the pressurizing piston.

In order to ascertain if these large conductivity changes brought about by pressure were reversible, particularly between atomspheric pressure and the pressure at which these conductivity experiments were performed, the following additional experiment was carried out. This experiment consisted of comparing the

TABLE I. Parameters for the constants in the polynomial, $t_P = t_0 + b_1 P + b_2 P^2$, representing the fusion curves of $HgCl_2$ and HgI_2.

Compound	t_0 (deg)	b_1 (deg/kbar)	b_2 (deg/kbar²)
$HgCl_2$	276	19.8	−0.26
HgI_2	259	17.1	−0.41
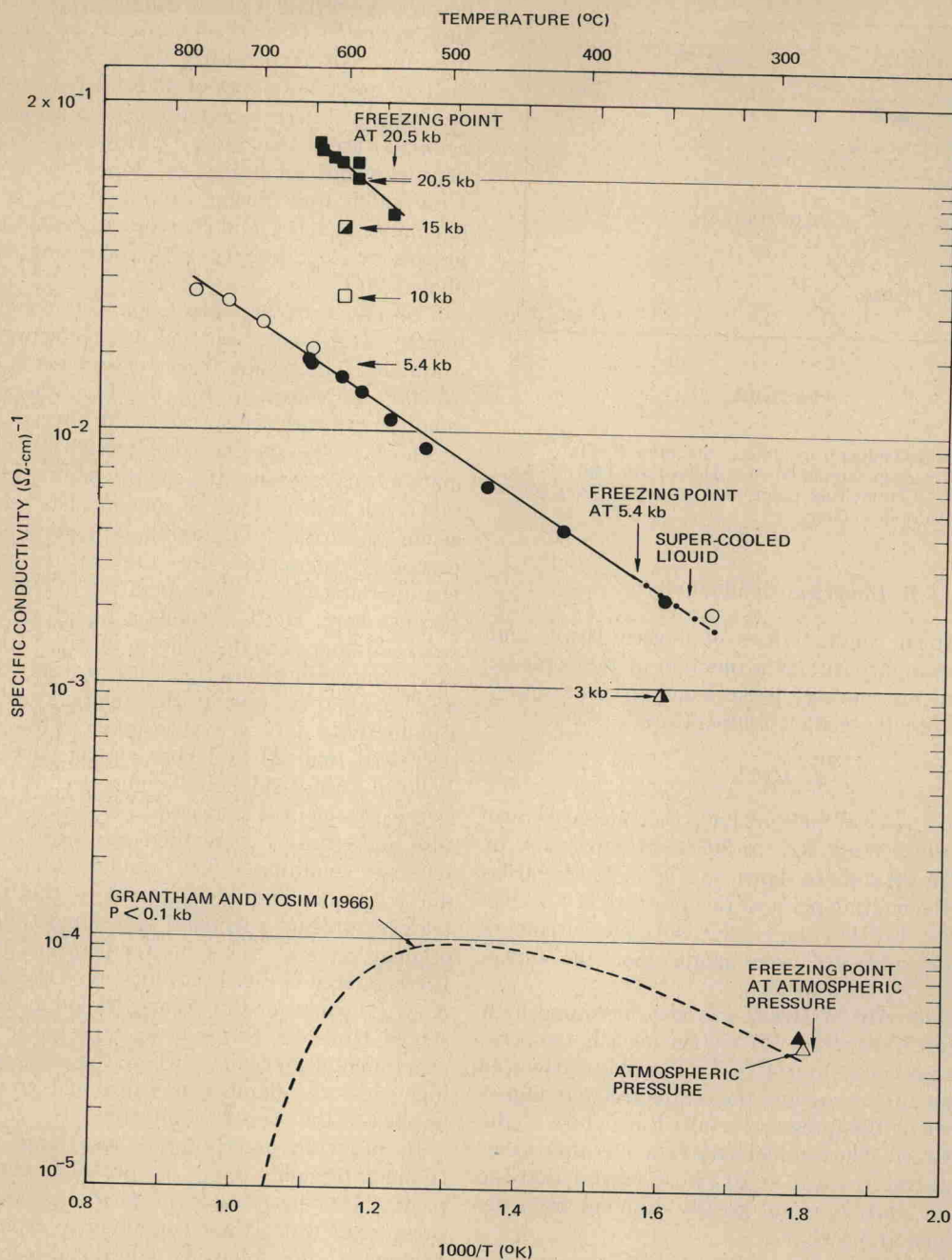
Fig. 3. $\log K (\Omega \cdot cm)^{-1}$ vs $1/T$ (°K) for HgCl₂ ($\triangle$) $P = 1$ atm, before pressurization; ($\blacktriangle$) $P = 1$ atm, after pressurization; ($\triangle$) $P = 3$ kbar; ($\bigcirc$) $P = 5.4$ kbar, Sample No. 1; ($\bullet$) $P = 5.4$ kbar, Sample No. 4; ($\square$) $P = 10$ kbar; ($\blacksquare$) $P = 15$ kbar; ($\blacksquare$) $P = 20.5$ kbar.

electrical conductivity of molten HgCl₂ at atmospheric pressure before and after it had been subjected to a pressure of 3 kbar. In order to do this, however, it was necessary to employ a different type of conductivity cell since the quartz cell after once having been subjected to high pressure cannot be returned to atmospheric pressure and still retain the liquid sample. A

Teflon conductivity cell, similar to the device described by Jayaraman et al.[17] was used to carry out this reversibility test. The conductivity of HgCl₂(l) was first measured at a pressure of one atmosphere at a temperature 5°C above the mormal melting point. This sample was then pressurized to 3 kbar and its conductivity measured at 350°C. (350°C is the upper tem-