



FIG. 6. Isothermal specific conductance (K) of HgI_2 as a function of pressure (kbar).

conducting salts has been measured over a large temperature interval ($\sim 500^\circ\text{C}$) at a constant, but high, pressure of 5.4 kbar.

The conductivity data at these elevated pressures obtained by Darnell *et al.* on the bismuth trihalides⁸ and upon the molten compounds of HgCl_2 and HgI_2 reported here would tend to support the suggestion made by Grantham and Yosim⁵ that these systems become more molecular with decreased density when heated at ordinary pressures. The increase in conductivity with pressure at constant temperature observed for these molten salts makes this idea attractive. Schlichtärle, Töheide, and Franck²¹ have shown on the other hand, that the electrical conductivity of the "strong" electrolyte NaNO_3 decreases with an increase in pressure. One might expect that this decrease in conductivity with increasing pressure is due to a decreased mobility of the ions of this strong electrolyte and not due to a decrease in the number of ionic carriers. In the case of BiX_3 and HgX_2 however, such a decrease in ionic mobility with an increase in pressure could easily be overcome by an increase in the number of ionic species. For example, in NaNO_3 an increase in pressure by 10 kbar decreases the conductivity to 0.62 of the conductivity at zero pressure. For HgCl_2 such an increase in pressure increases the conductivity of the liquid by a factor of 5. For HgI_2 this ratio is 2.5. Thus the enhancement in electrical conductivity with an increase in pressure appears to be greater for salts that are more molecular at ordinary pressures, i.e., $K_{P=10\text{kbar}}/K_{P=0}$ decreases in the sequence $\text{HgCl}_2 > \text{HgI}_2 > \text{NaNO}_3$. These data suggest that the K vs P curve for a weak

electrolyte may perhaps exhibit a maximum at sufficiently high pressures where the two opposing pressure coefficients (increased ionization and decreased mobility) become comparable. The K vs P curve for BiCl_3 ⁸ suggests that such a maximum may exist.

Thus these results show that pressure brings about a large change in the electrical conductivity of the mercuric halides, HgCl_2 and HgI_2 . For example, in the former case an increase in pressure from near atmospheric to 20 kbar brings about an increase in conductivity of over three orders of magnitude. In the case of HgI_2 , pressurization to 5 kbar changes the sign of the temperature coefficient of conductivity from its anomalous negative value at zero pressure to a positive temperature coefficient whose Arrhenius activation energy for conduction is comparable to that of a strong electrolyte, i.e., 2.5 kcal/mole.

ACKNOWLEDGMENT

The authors wish to acknowledge the many valuable discussions with Dr. S. J. Yosim during the course of this work.

* This work was supported by the Research Division of the U.S. Atomic Energy Commission.

¹ W. Klemm and W. Biltz, *Z. Anorg. Allgem. Chem.* **152**, 225 (1926).

² J. O. M. Bockris, E. H. Crook, H. Bloom, and N. E. Richards, *Proc. Roy. Soc. (London)* **A255**, 558 (1960).

³ G. J. Janz and J. E. E. McIntyre, *J. Electrochem. Soc.* **109**, 842 (1962).

⁴ G. V. Hevesy, *Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd.* **3**, 13 (1921).

⁵ L. F. Grantham and S. J. Yosim, *J. Chem. Phys.* **45**, 1192 (1966).

⁶ L. F. Grantham and S. J. Yosim, *J. Phys. Chem.* **67**, 2506 (1963).

⁷ L. F. Grantham and S. J. Yosim, *J. Phys. Chem.* **72**, 762 (1968).

⁸ A. J. Darnell, W. A. McCollum and S. J. Yosim, *J. Phys. Chem.* **73**, 4116 (1969).

⁹ L. F. Grantham, *J. Chem. Phys.* **49**, 3835 (1968).

¹⁰ A. J. Darnell and W. A. McCollum, *J. Phys. Chem.* **72**, 1327 (1968).

¹¹ F. P. Bundy, in *Progress in Very High Pressure Research*, edited by F. P. Bundy, W. R. Hibbard, and H. M. Strong (Wiley, New York, 1961), p. 256.

¹² P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **51**, 55 (1915).

¹³ J. W. Brasch, A. J. Melveger, and E. R. Lippincott, *Chem. Phys. Letters* **3**, 99 (1968).

¹⁴ G. J. Janz and J. D. E. McIntyre, *Ann. N. Y. Acad. Sci.* **79**, 761 (1960).

¹⁵ L. E. Topol and L. D. Ransom, *J. Phys. Chem.* **64**, 1339 (1960).

¹⁶ G. C. Kennedy and R. C. Newton, in *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill, New York, 1963), p. 167.

¹⁷ A. Jayaraman, A. R. Hutson, J. H. McFee, A. S. Coriell, and R. G. Maines, *Rev. Sci. Instr.* **38**, 44 (1967).

¹⁸ B. R. Sundheim, *Fused Salts* (McGraw-Hill, New York, 1964), p. 36.

¹⁹ L. F. Grantham, E. B. Harrelson, P. H. Shaw, and C. M. Larsen, *Rev. Sci. Instr.* **39**, 699 (1968).

²⁰ S. J. Yosim (private communication).

²¹ G. Schlichtärle, K. Töheide and E. V. Franck, *J. Chim. Phys. Physicochim. Biol.* **1969**, 70-4.

