

FIG. 5.—Conductivity isotherms for HgI_2 ; ●, increasing pressure; ■, decreasing pressure. From top to bottom, the temperatures are: 276, 287, 310, 332 and 368°C.

HgCl_2 at atmospheric pressure agree with those of ref. 1 and 7 within 1 %. For HgBr_2 , our results are about 4 % below those of ref. 1, 6 and 7. This small discrepancy may be due to differences in sample purity.

POSSIBILITY OF ELECTRONIC CONDUCTIVITY

Before interpreting these results, we wished to show by experiment whether electronic conductivity contributes significantly to the total conductivity. This point

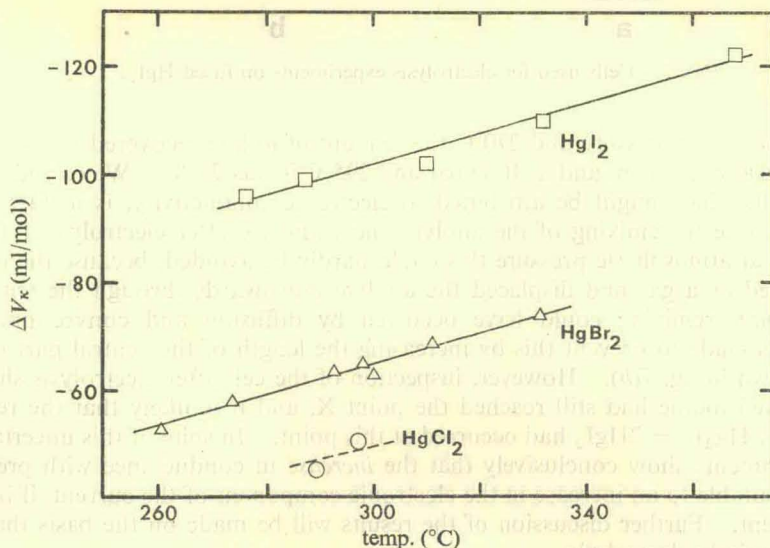


FIG. 6.—Plots of ΔV_κ against temperature for the fused mercuric halides.

was considered by Grantham and Yosim,¹ and also by Janz and McIntyre,⁶ who concluded that electronic conductivity is unlikely to be significant at atmospheric pressure. However, it is known that TlI and SnI₄ become electronically conducting at very high pressures in the solid state,^{8, 9} and it was thought possible that the large increase in conductivity with pressure observed for HgI₂ might be due to this cause. Direct current was passed through molten HgI₂, and the amount of chemical change compared with that predicted by Faraday's laws of electrolysis. Since an electronic component of the current would produce no chemical change, the Faradaic yield is equal to the fraction of the current which is electrolytic (under which heading we include charge flow by a Grotthus mechanism). The experiment was performed at atmospheric pressure and at 1000 bar. The electrolysis cells are illustrated in fig. 7. In each case the left-hand electrode was the anode, where iodine was liberated. Mercurous iodide was formed at the cathode. The amount of electricity passed was measured with a coulometer in which water was decomposed to hydrogen and oxygen. Currents between 2 mA and 12 mA were used, and about 4×10^{-4} equivalents of iodine were liberated. After electrolysis, the anode compartment was broken, the contents dissolved in potassium iodide solution and the iodine titrated with thio-sulphate.

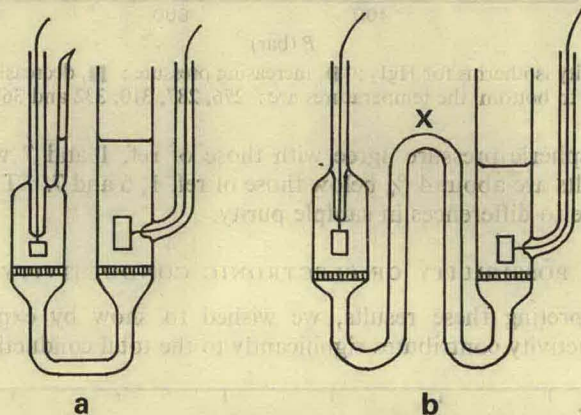


FIG. 7.—Cells used for electrolysis experiments on fused HgI₂.

At atmospheric pressure and 270°C the amount of iodine recovered was 84 % of the theoretical maximum, and at 1000 bar and 295°C it was 78 %. We consider that the shortfall, which might be attributed to electronic conductivity, is in fact more likely to be due to remixing of the anolyte and catholyte after electrolysis. In the experiment at atmospheric pressure this could hardly be avoided, because the iodine was liberated as a gas and displaced the anolyte downwards through the frit. At high pressure, remixing could have occurred by diffusion and convection. An attempt was made to prevent this by increasing the length of the central part of the cell, as shown in fig. 7(b). However, inspection of the cell after electrolysis showed that dissolved iodine had still reached the point X, and it is likely that the reverse reaction $I_2 + Hg_2I_2 = 2HgI_2$ had occurred at this point. In spite of this uncertainty, these experiments show conclusively that the *increase* in conductance with pressure is *not* attributable to an increase in the electronic component of the current, if indeed this is present. Further discussion of the results will be made on the basis that the current is entirely electrolytic.