away from the cell condensed on the lower part of the inside wall of this tube, and was thus prevented from reaching the walls of the pressure vessel. The thermocouple and the conductivity cell leads were similarly protected by glass tubes. The conductivity cell contained platinized platinum electrodes of the " ring and rod " type, this configuration being chosen because it makes the cell constant relatively insensitive to dimensional changes in the cell caused by slight distortion during pressure cycling.[5] Cell constants were about 0.5 cm^{-1}, and were measured before and after each run using 0.01 Demal KCl solution at 25.0°C. The cell constant changed by about 0.3 % between room temperature and 330°C (the highest temperature used). Salt was loaded into the cell as a cast stick, and a glass insert placed on top of it. The insert floated on the molten salt, reducing the exposed surface to a narrow annulus. This lowered the rate of evaporation to an acceptable level, and also restricted the rate of diffusion of dissolved gas into the region between the electrodes. No hysteresis in the conductivity was observed during pressure cycles, indicating that gas dissolution did not influence the results significantly.

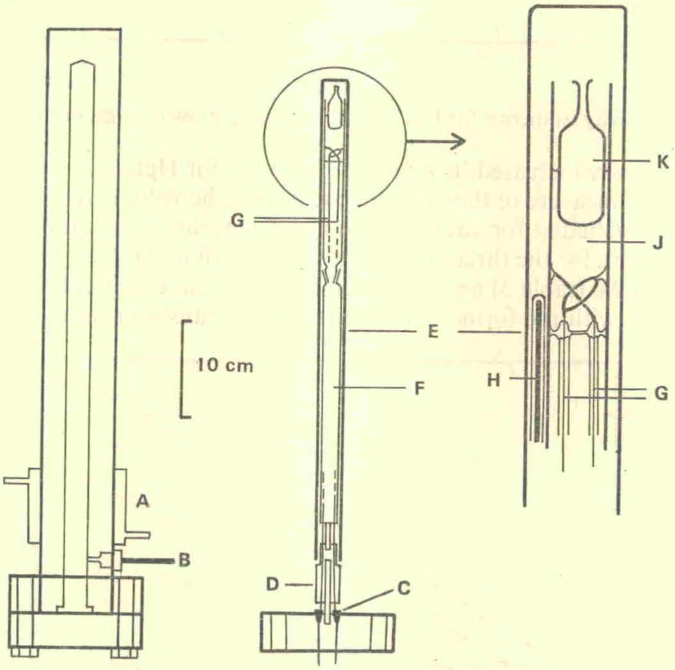

FIG. 2.—Pressure vessel, insert and conductivity cell used for $HgCl_2$ and $HgBr_2$. A, water jacket; B, inlet for high pressure gas; C, Bridgman cones for electrical leads to cell and thermocouple; D, pyrophyllite insulator; E, outer glass tube; F, glass column; G, platinum leads, in glass sheaths; H, stainless steel clad thermocouple, in glass sheath; J, melt; K, glass float.

Conductances were measured with a Wayne-Kerr transformer ratio-arm bridge (type B 221), using an external oscillator (Advance, type J 1) and tuned amplifier null detector (General Radio, type 1232 A). Measurements were made over the frequency range 1 to 10 kHz. Between these limits, the conductivity varied by less than 0.1 %. The usual extrapolation to infinite frequency was considered to be unnecessary, in view of the comparatively large changes in conductivity with pressure.

RESULTS

Fig. 3, 4 and 5 show isothermal plots of log (conductivity) against pressure for HgI_2, $HgBr_2$ and $HgCl_2$. When the pressure was raised from atmospheric to 1000

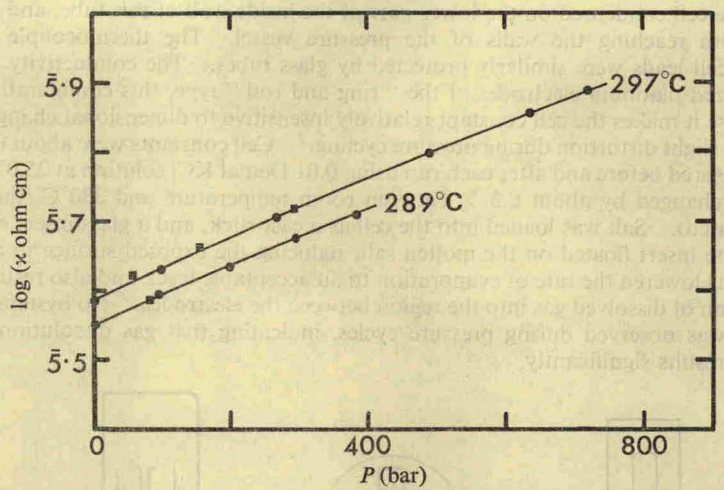

FIG. 3.—Conductivity isotherms for $HgCl_2$; ●, increasing pressure ; ■, decreasing pressure.

bar, the conductivity increased by a factor of about 6 for HgI_2, 3.5 for $HgBr_2$ and 2.5 for $HgCl_2$. As a measure of the pressure coefficient, the volume $\Delta V_\kappa = -RT(\partial \ln \kappa/\partial P)_T$, has been evaluated for each isotherm at atmospheric pressure. Plots of ΔV_κ against temperature for the three compounds are shown in fig. 6. (The symbols ΔV_κ, and later E_P and E_V (table 3) are used in this paper in an empirical sense only ; they are not identified with the formation of a particular transition state).

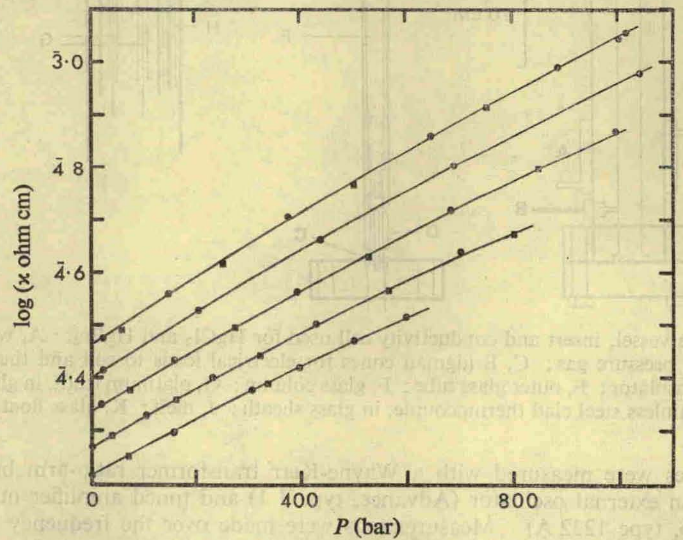

FIG. 4.—Conductivity isotherms for $HgBr_2$; ●, increasing pressure ; ■, decreasing pressure. From top to bottom, the temperatures are 331.5, 311, 292.5, 273.5 and 260.5°C.

DISCUSSION

COMPARISON WITH PREVIOUS WORK

The conductivities of the fused mercuric halides have been measured by Grantham and Yosim,[1] Janz and McIntyre [6] and Bockris *et al.*[7] Our results for HgI_2 and