

EXPERIMENTAL

MATERIALS

AgCl and AgBr were prepared in a dark room, by treating aqueous AgNO₃ solution (B.D.H., A.R.) with HCl or HBr solution (B.D.H., A.R.). The precipitates were collected and washed with dilute HCl or HBr, followed by distilled water. They were dried in an air oven at 150°C for several days. KCl, KBr, KI, NaCl and NaBr (B.D.H., A.R.) were recrystallized from distilled water. The solutions were evaporated to dryness at 80°C, and the salts were finally dried by gradually heating them to 300°C over 48 h. NaI, RbCl, RbI, CsCl, CsBr and CsI were similarly prepared from B.D.H. reagent-grade chemicals (99 % pure). LiCl, LiBr, and LiI were made by treating a filtered solution of Li₂CO₃ with HCl, HBr or HI (A.R.). The solutions were evaporated to dryness at 80°C, and the solids were dried under vacuum as the temperature was slowly raised to 100°C over 24 h and then to 350°C over 24 h. Solutions of all alkali halides gave a neutral reaction both before and after conductivity measurements.

HIGH PRESSURE APPARATUS

The pressure vessel was made from Nimonic 105 (H. Wiggin & Co., Hereford, England). It was of 2.5 cm i.d., 7.5 cm o.d. and 75 cm long, and was mounted vertically. The upper end was heated by an external furnace. The furnace windings were in three sections, which were shunted by rheostats. These were adjusted to give an isothermal zone of length 6 cm, the centre of which was 12 cm from the top of the bore. The temperature profile in this zone did not change when the pressure was raised from atmospheric to 1000 bar. At the lower end, the vessel was cooled by a water jacket, below which was a flange closure and rubber O-ring seal. The lower flange carried a port for admission of argon, and six electrical terminals insulated by conical Nylon sleeves. Four of these terminals were of mild steel, and were used to make connections to the conductance cell; the remaining two were of chromel and alumel, and were connected internally and externally to wires of these metals. The internal wires were insulated with alumina sleeving. The thermocouple junction was positioned opposite the centre of the conductivity cell, and was protected by a silica sheath. An isothermal pressure change of 1000 bar causes the e.m.f. of the chromel-alumel couple to change by less than 5 μ V.⁷ Neglect of this would cause an error of 0.1 K in temperature measurement, which is negligible. Pressures were measured to ± 5 bar with a Bourdon gauge (Budenberg Gauge Co., Ltd.) which was calibrated against a dead-weight tester. Argon (99.9 %) was taken directly from cylinders and compressed to the working pressure by a diaphragm compressor (Pressure Products Ltd., model 3033).

CONDUCTANCE CELLS AND BRIDGES

Various conductance cells were used, employing Pyrex, silica, hot pressed alumina or sapphire as construction material, with platinum electrodes (see fig. 1). For each cell, diffusion of dissolved gas from the exposed surface of the melt into the region between the electrodes was hindered by restricting the intervening melt to a narrow annular space between the cell and the tube surrounding it. Pyrex cells (fig. 1a) were used for the silver halides, silica cells (fig. 1b) for the halides of Na, K, Rb and Cs, and alumina or sapphire cells (fig. 1c) for the lithium halides. The cell was held in a stainless steel or silica cup, positioned in the isothermal zone of the pressure vessel. The cup was supported on a column of pyrophyllite spacers, threaded onto a central rod of stainless steel. An inverted silica tube was placed over the cell, with the open end extending downwards into the cold part of the vessel. This tube protected the walls of the pressure vessel from attack by corrosive salt vapours.

Conductances were measured with a transformer ratio-arm bridge (Wayne-Kerr, type B221), with external audio-oscillator and tuned amplifier and null detector, or with a Jones bridge which has been described previously.¹ The lead resistances were determined as a function of temperature and pressure, and appropriate corrections were applied. Conductance measurements were made over a range of frequencies (2-10 kHz) and were corrected to infinite frequency.¹ The frequency dependence was generally less than 1 % over this range, and was independent of temperature and pressure for a given salt and cell.

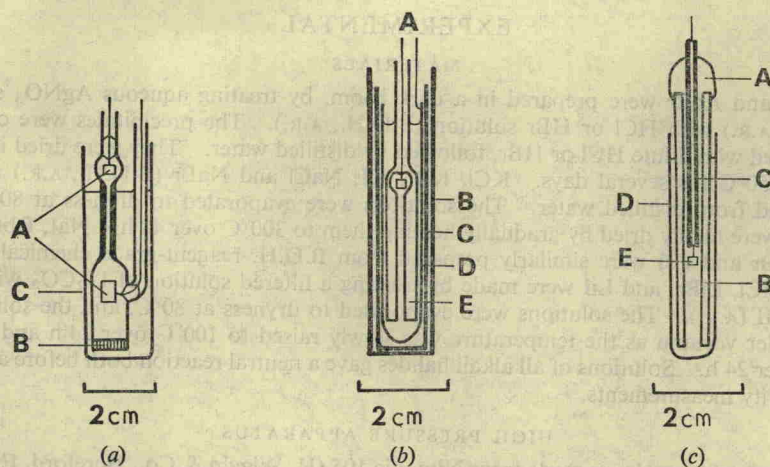


FIG. 1.—Conductance cells. (a) Pyrex cell; A, platinum electrodes; B, porosity 3 frit; C, Pyrex tube. (b) Silica cell; A, platinum leads; B, stainless steel cup; C, silica tube; D, platinum container and electrode; E, silica capillary. (c) Alumina or sapphire cell; A, alumina bead fused on; B, alumina or sapphire capillary; C, alumina tube; D, platinum container and electrode; E, inner platinum electrode.

PROCEDURE FOR CONDUCTANCE MEASUREMENTS

The cell was loaded with dried, powdered salt, and was put into the cup on the pyrophyllite support column. The silica tube was placed over this, and the whole unit was pushed up into the pressure vessel (which was at the required working temperature). The vessel was sealed, and a suitable time was allowed for the cell and vessel to reach temperature equilibrium (ca. 1 h). The pressure was raised in stages to 1000 bar, and then reduced again to atmospheric, readings being taken at each pressure. A complete pressure cycle lasted about 90 min, after which time the melt was allowed to degas at atmospheric pressure for 2-3 h. At the end of a set of experiments, the contents of the cell were dissolved in water and treated with phenolphthalein, to confirm the absence of hydrolysis or oxidation products.

MEASUREMENT OF $(\partial P/\partial T)_V$

Thermal pressure coefficients were calculated from literature values of the expansivity and compressibility for most of the compounds studied, using eqn (3). $(\partial P/\partial T)_V$ was measured directly for AgCl, AgBr and CsI, for which no compressibility data were available, and also for CsCl. A pycnometric method was used, the pycnometers being made from Pyrex for AgCl and AgBr (fig. 2a) and from silica for CsCl and CsI (fig. 2b). In each version, a capillary stem of length 10 cm and 1 mm i.d. was provided, to reduce the rate of diffusion of dissolved gas from the meniscus into the bulb. The Pyrex cell had a platinum wire sealed through the bottom, and a second wire could be inserted into the top of the capillary. In the silica cell, a twin-bore capillary was used, into which wires were inserted to different depths. In both cases, contact between the meniscus and the upper probe was indicated by an abrupt drop in the electrical resistance between the probes. The cells were filled by charging the upper chamber with purified, powdered salt. The salt was melted, and forced into the lower bulb. The filling chamber was then broken off, the probe wires were inserted and the cell was mounted inside the pressure vessel. The temperature was raised slowly (2-3 K/min) until the meniscus contacted the upper probe. The temperature was noted, and the pressure was increased to a new value. The temperature was again raised slowly, until contact with the upper probe was re-established. This situation could be detected with a precision which varied from $\pm \frac{1}{4}$ K to ± 1 K. These operations were repeated until the pressure reached 1000 bar. Checks were made for the absence of irreversible effects due to leakage, evaporation, chemical change or gas dissolution. Plots of P against T were straight lines within