

high strength steel is chosen. The outer surface of the pressure vessel is equipped with a water cooling system to keep the wall of the vessel at low temperatures. The bore of the pressure vessel is closed by Bridgman seals at either end.

The internal furnace (Fig. 2) consists of four independently controlled resistance heaters made of molybdenum wire insulated by thin-walled alumina tubes. Between the furnace and the wall of the pressure vessel zirconia, fired, and unfired pyrophyllite tubings are inserted for thermal insulation purposes. In order to avoid convection in the pressure transmitting compressed argon the insulating tubes fit smoothly and the gaps between them are sealed by O-rings at the upper end. In addition all cavities are filled carefully with alumina powder. The complete furnace is connected to the lower Bridgman plug through which the electrical leads enter the high-pressure chamber. Small electrically insulated Bridgman plugs made from copper-beryllium bronze which are positioned in inclined bores in the lower Bridgman plug serve as feed-throughs for the power leads.

The temperature is measured by three sheathed chromel-alumel thermocouples distributed along the volumometer. They enter the pressure vessel at a

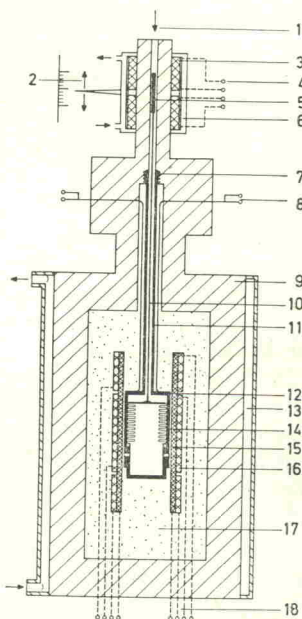


Fig. 1. Schematic diagram of high pressure apparatus: 1 gas inlet; 2 micrometer screw; 3 differential transformer; 4 leads to carrier frequency amplifier; 5 ferromagnetic tip; 6 thermostat; 7 fixed point of suspension system; 8 thermocouple inlets; 9 pressure vessel; 10 wire; 11 suspension tubing; 12 bracket; 13 cooling jacket; 14 volumometer with bellows; 15 main heater; 16 auxiliary heaters; 17 thermal insulation; 18 power leads.

position indicated in Fig. 1 through small Bridgman plugs into which they are soldered. The thermocouples are calibrated at the melting points of antimony and silver according to the International Practical Temperature Scale of 1968 (Sb: 630.74 °C; Ag: 961.93 °C) and at the melting point of KCl for which the value $T_F = 770.3$ °C of Roberts⁴ is chosen which was confirmed by Johnson and Bredig⁵ and was used in recent studies^{6, 7}.

The accuracy of temperature measurement including errors caused by temperature inhomogeneities is ± 2 K.

The vessel is pressurized by compressed argon. A two-stage diaphragm gas compressor (Nova) compresses argon from commercial cylinder supplies into the pressure vessel through the upper Bridgman

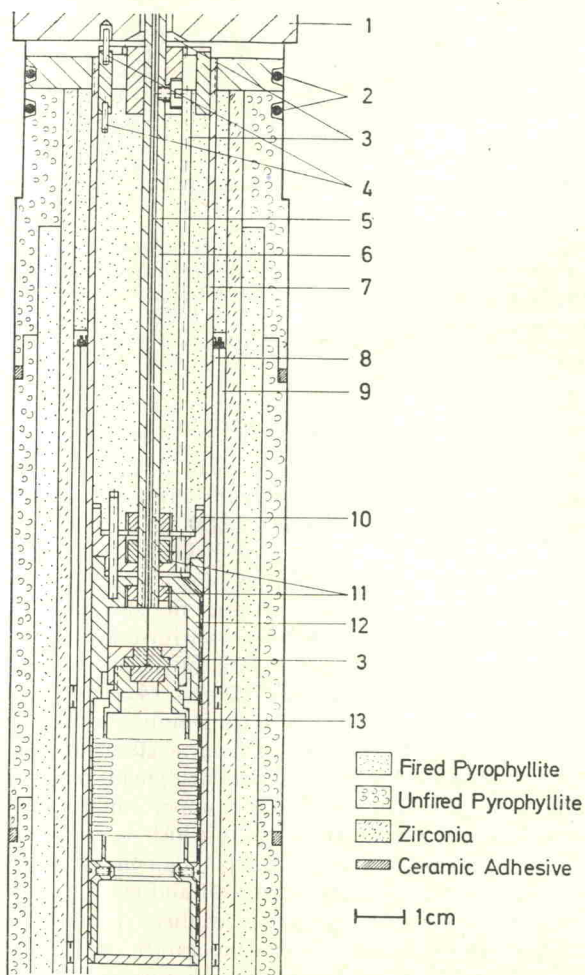


Fig. 2. Volumometer, heaters, and insulation: 1 upper Bridgman plug; 2 O-rings; 3 thermocouples; 4 anti-torsion pins; 5 wire; 6 suspension tubing; 7 inner tube of furnace; 8 main heater; 9 auxiliary heaters; 10 centering device; 11 nuts; 12 bracket; 13 volumometer with bellows.

plug and into a pressure intensifier (Autoclave Engineers) to pressures of 3000 bar. Higher pressures are generated by the intensifier operated by an air-driven hydraulic pump.

The gas pressure is measured by a set of Bourdon gauges (Heise) with ranges of 1000, 3000, and 7000 bar and an accuracy of 0.1% of full scale reading. The gauges are calibrated against a dead-weight tester.

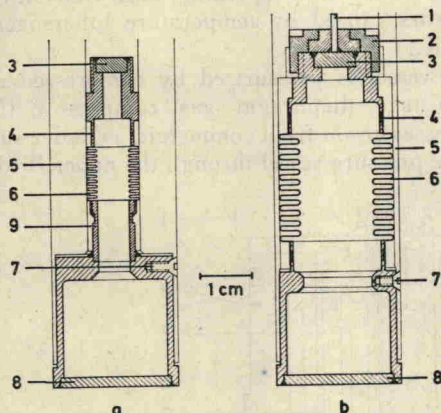


Fig. 3. Volumometers for different density ranges: a) type 1 for low densities, b) type 2 for high densities. 1 wire for displacement measurement; 2 gland; 3 lid (argon welded); 4 welded seam; 5 bracket; 6 metal bellows; 7 screw; 8 bottom part; 9 spacer.

2.2 Volumometer

The volumometer shown in Fig. 3 is a closed system of fixed salt content consisting of a rigid stainless steel cell (Remanit 1880 SST, Deutsche Edelstahl-Werke) and a metal bellows (material: Inconel 600, Henry Wiggin and Co.) which allows for pressure equilibration between the salt and the pressurizing argon. Metal bellows with different diameters are used depending on the density range leading to volumes between 7.2 and 14.3 cm³. The lower end of the volumometer is rigidly attached to a bracket which is suspended from a stainless steel tubing connected to the upper Bridgman plug as indicated in Figure 1. To the upper end of the volumometer a wire is attached which is made of the same material as the tubing, thus compensating for most of the thermal expansion and compression effects along the temperature gradient from measuring temperature to room temperature and in the upper Bridgman seal. The wire is carrying a ferromagnetic tip. Hence changes in volume of the volumometer can be measured via displacements of its upper end by a thermostatted differential transformer outside the high-pressure system which can be

moved up and down by a micrometer screw to find the relative zero position with respect to the ferromagnetic tip, which is monitored by a carrier frequency amplifier (Hottinger Meßtechnik). With this experimental set-up it is also possible to carry out quasi-isochoric measurements by adjusting the pressure in a way that the upper end of the volumometer is kept at the same (zero-)position when the salt is heated or cooled slowly.

Since the suspension system described above does not compensate for all expansion and compression effects completely, the small resultant erroneous zero point shift of the arrangement is determined by replacing the volumometer by a solid piece of metal of the same material and size and then measuring the movement of the ferromagnetic tip as a function of pressure and temperature. The resultant shift which is found to be reproducible to ± 0.07 mm with an additional uncertainty of 0.07 mm for the zero point position is taken into account as a correction to the displacements measured. The uncertainty in the final density values caused by this effect is only small for volumometers of type 1, but it is appreciable (0.25%) for type 2 volumometers. In this case it can be diminished by finding the zero point position with the aid of density values obtained with type 1 volumometers (see also Sect. 2.4 and Table 1).

2.3 Experimental Procedure

The zero point volume at 20 °C of the volumometer is determined before an experiment by differential weighing with water and carbon tetrachloride. The salt (E. Merck and Co., >99.5%) is dried carefully under vacuum at about 450 °C for at least six hours⁸, then fused in a quartz glass funnel and introduced into the volumometer. After filling and cooling down the volumometer the amount of salt is determined by differential weighing. Then the volumometer is closed by welding under dry argon gas and placed into the pressure vessel.

For densities smaller than the density of the fused salt at its melting point at 1 bar pressure cells of type 1 (Fig. 3) are used. They are heated at ordinary pressure until the salt fills the zero point volume of the volumometer completely. Upon further heating the pressure is adjusted in a way, that a quasi-isochoric measurement can be performed. For densities higher than the density of the liquid at its ordinary melting point volumometers of type 2 are chosen because the larger bellows allow for the volume increase of the salt upon fusion without irreversible deformations caused by large elongations. In order to check the consistency of the isochores in this range additional isothermal mea-