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In order to study phase equilibria in aqueous systems at high temperatures, a diamond-anvil cell that can be loaded with compressed-gas mixtures and a matching thermostat were developed. Care was taken to ensure a stable (0.1 K) and homogeneous (<0.5 K) temperature distribution inside the cell by using a two-stage heating system. Experiments were performed up to 50 kbar at 650 K on pure nitrogen. The observed melting line of nitrogen is in very good agreement with previous results.

I. INTRODUCTION

Research on fluid binary mixtures with water as one of the components is of interest for several reasons. First, our knowledge of simple nonpolar fluid mixtures is increasing steadily.[1] An important extension of this research is to binary mixtures with one polar component, of which water is an archetype. Second, water forms solids with very open structures that can contain other molecular species, so-called clathrates. Physically interesting topics of these systems are, e.g., the mobility of the guest molecules, the formation of clusters, the existence of decomposition pressure, and the influence of a phase transition in the host structure. Finally, there are important applications for aqueous systems to geological and chemical processes and to the modeling of planetary atmospheres. The phase behavior of fluid mixtures containing water has been investigated up to 700 K and 2.5 kbar by Wu *et al.* (see, e.g., Ref. 2). In order to extend these measurements to higher pressure, we have developed a diamond-anvil cell (DAC), suitable for at least 850 K, and a pressure vessel for loading the DAC at a temperature in excess of 647 K (the critical temperature of water) in order to keep the gas mixture homogeneous. Here, only the DAC will be described. A preliminary report has appeared in Ref. 3.

Previously, a DAC for fluid mixtures and a loading system at ambient temperature were developed[4] and used in our laboratory up to 530 K and 240 kbar. From our experience with this cell, a number of requirements were posed on the new high-temperature DAC (named HT-DAC).

(i) The gradients in the sample space should be small (typically <1 K), since, with larger gradients, different phase equilibria may occur simultaneously in the sample space. This would make it impossible to draw conclusions about the situation in thermodynamic equilibrium.

(ii) The cell should fit a thermostat where the temperature is regulated to within a few Kelvin and measured with a comparable precision to establish the many possible phase equilibria.

(iii) The thermostat should provide optical access from two opposite sides for visual observation of the sample, ruby fluorescence measurements, Raman scattering, and interference measurements.

(iv) The cell should be small enough to be placed in the existing pressure equipment in order to be loaded with a compressed homogeneous fluid mixture.

(v) The pressure should be tunable at high temperature, without having to cool the system to room temperature.

(vi) High temperature requires a careful selection of the materials to be used for the construction of various parts of the system.

Since we felt that these requirements could not be met by the high-temperature cells already described in the literature,[5–8] it was decided to develop a new one. In the following section, the design of the high-temperature cell and its thermostat is presented. In Sec. III the performance of the apparatus is tested.

II. APPARATUS

The design of the HTDAC is shown in Fig. 1. In the figure, a cross section through the plane parallel to the long axis and the optical axis is presented. The central part is a Bassett-type[9] cell, in which one of the two diamonds (11) is mounted on a piston (23) that is driven by a nut (3). The diamond is clamped with a platinum ring (6) on a hemisphere (5). A plane-parallel orientation of the diamonds is ensured by rotating the hemisphere. This can be accomplished by the screws (10), that push on a ring (20) that in its turn pushes on the hemisphere. To prevent the piston from rotating, it is kept in a fixed orientation by inserting a screw (21) in a groove in the piston. The upper diamond is clamped with a platinum ring (17) in a holder (7), that is, in its turn, fixed in the housing (4) through screws (12). The holder can be translated by screws (9) to position the diamonds above each other, after the screws (12) have been slightly loosened. The optical apertures have full angles of 25°, as seen from the sample space.

In order to load the cell with a mixture of known composition, the cell is placed in a pressure vessel to fill it with a homogeneous gas mixture. The diamonds are closed on the gasket (19)—that contains the sample space—by

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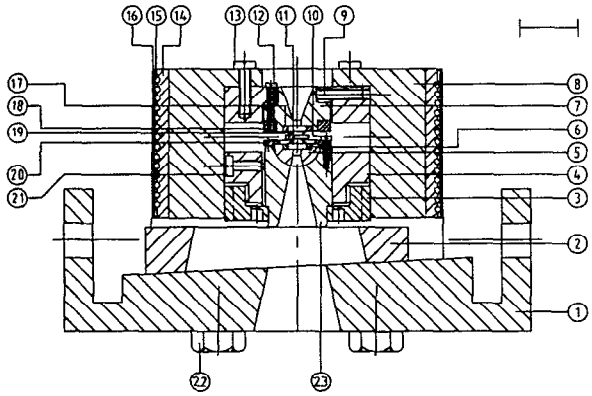

FIG. 1. Cross section of the HTDAC through the plane parallel to the long axis and the optical axis. The bar (top right) indicates a length of 1 cm. The numbers denote the following components. 1: main bed; 2: wedge; 3: nut; 4: housing; 5: hemisphere; 6: clamping ring; 7: holder; 8: main body; 9: translation screws; 10: screw; 11: diamond; 12: holding screws; 13: holding screws; 14: cylinder; 15: heating coil; 16: cylinder; 17: clamping ring; 18: ring; 19: gasket; 20: tilting ring; 21: screw; 22: bolt; 23: piston.

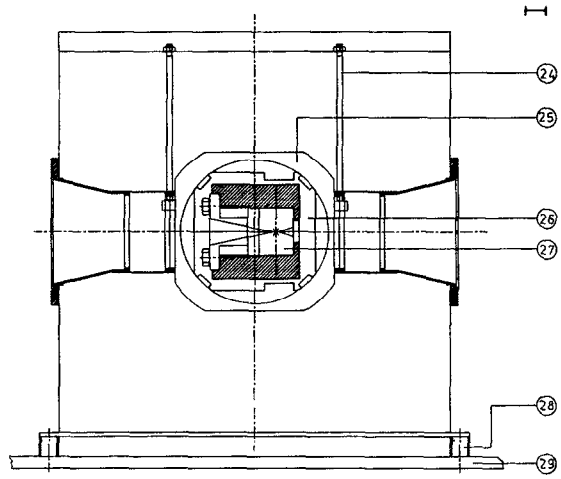

FIG. 2. Cross section through the plane that is parallel to the optical axis and parallel to the vertical axis of the cell. The bar (top right) indicates a length of 1 cm. The numbers denote the following components. 24: rod; 25: main cylinder; 26: spacer; 27: diamond-anvil cell; 28: spacer; 29: plate.

turning the nut (3) from outside the vessel. Once the cell is loaded, it is fixed in the cylindrical main body (8 in Fig. 1) with screws (13). At the lower side of the main body, the rectangular bed (1) is connected with bolts (22). A rectangular wedge (2), with an angle of 3°, slides on the bed. Since the piston protrudes from the nut (3), the pressure can be adjusted by pushing on the wedge, which in its turn pushes the piston. A wedge system was chosen rather than a nut as in the MDAC (Ref. 4), because less force is needed to change the pressure. The cell is machined from heat-resistive alloy Inconel 718, except the screw and the bolts, which are of stainless steel. A heating coil (15, Thermocoax S. A., France) is wound in grooves in a cylinder (14), that is mounted around the main body and kept in place by another cylinder (16). This allows a quick replacement of the heating coil if necessary.

In order to keep a homogeneous and fixed temperature, the HTDAC is placed in the thermostat box shown in Figs. 2 and 3. Figure 2 shows a cross section parallel to the optical and the vertical axes. It shows how the cell (27) is placed in the main cylinder (25) in a spacer (26). The cylinder is suspended from the top of the box on rods (24). The outside of the box reaches about 400 K when the cell is at a temperature of 850 K. Therefore, an extra plate (29) is mounted below the thermostat, separated from the box by four spacers (28), to protect the precision translation stages on which the box is mounted.

Figure 3 is a cross section through the horizontal plane of the thermostat. The HTDAC is inserted through the glass cylinder (27) into the main cylinder (25), where it is held by two spacers (26). The cylinder is closed by two covers (28 and 29). A heating coil (Thermocoax) is wound around the main cylinder. The coil is more densely wound near the covers of the cylinder and near the windows (31) to compensate for the heat losses through these parts. The optical axis is indicated with the vertical dash-dotted line. Three pairs of windows (Suprasil, low fluorescence) are placed on each side to reduce heat transfer by convection: One pair (31) is mounted in the cylinder, one pair (32) halfway between the cylinder and the box, and one pair (33) in the wall of the box. The small cylinder between windows 31 and 32 is machined of a heat-insulating ceramic (Macor) and the conical cylinder between windows 32 and 33 is of thin steel since window 32 is fixed in it. All windows can be accessed through the optical ports. The space outside the main cylinder and the optical apertures, including the glass cylinders (27, 30, and 34), is filled with flocks of insulating material (Kao-Wool).

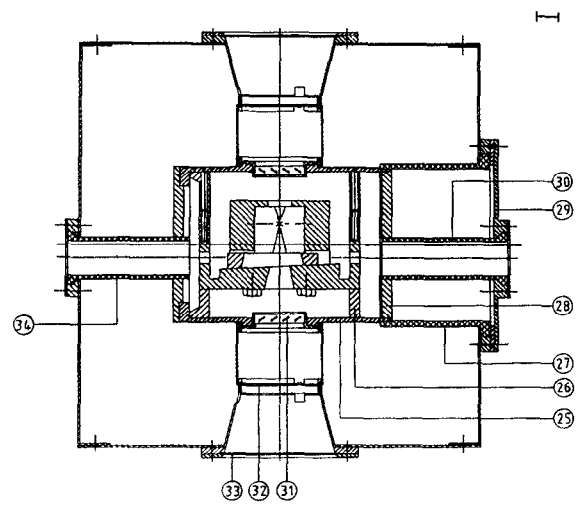

FIG. 3. Cross section of the HTDAC through the horizontal plane, parallel to the optical axis of the thermostat. The bar (top right) indicates a length of 1 cm. The numbers denote the following components. 25: main cylinder; 26: spacer; 27: glass cylinder; 28: cover; 29: cover; 30: glass cylinder; 31: quartz window; 32: quartz window; 33: quartz window; 34: glass cylinder.

The pressure in the cell is adjusted as follows: Outside the box is a yoke (not shown in Figs. 2 and 3) that holds two micrometer-driven rods. These rods are inserted through the glass cylinders (30 and 34). One rod pushes against the wedge while the other supports the bed of the wedge. Once the pressure is changed to satisfaction, the rods are taken out and the glass cylinders are refilled with insulating flocks. In this way, no strong permanent supports of the cell are needed. These supports usually involve a large heat flux and thus cause large temperature gradients. Release of the pressure in the cell is prevented by the friction between the wedge and the other parts.

In the high-pressure experiments, the temperature in the cell was measured with a calibrated[10] chromel-alumel thermocouple of 0.25 mm diameter (Thermocoax). The head of the thermocouple was inserted in a tight-fitting hole in the holder of the upper diamond. The hole is drilled as far as possible towards the diamond. On the top of the main body, the thermocouple is fixed with a few loops under a metal flange to provide good thermal coupling of the thermocouple to the cell.

As mentioned before, the system is heated by two heating coils. The one around the large cylinder is fed by a 160-W power supply and provides the main temperature regulation. It is controlled with a platinum resistor. The coil around the diamond cell is fed by a 10-W supply and has the task to smooth the temperature gradients inside the main cylinder and to smooth possible temperature variations of the large power supply. It is controlled by a differential thermocouple, referenced at the heating coil of the main cylinder.

The thermostat box is permanently flushed with argon, to reduce oxidation of those parts of the cell that are at high temperature (especially the diamonds). The gas is fed at the bottom of the box. Also, a radiation shield is placed in the insulation halfway between the main cylinder and the box.

III. TEST OF THE EQUIPMENT AND DISCUSSION OF THE RESULTS

In this section, experiments are described to test the design of the cell. In the first series of experiments, the temperature gradients in the cell were measured at temperatures up to 850 K without a sample in the cell. In the second series of experiments, the cell was loaded with nitrogen and experiments up to 50 kbar and 650 K were performed.

The most important temperature gradients are those around the sample space. Therefore, homemade iron-constantan thermocouples were put between the diamonds (instead of the sample), under the bolts (22 in Fig. 1), and on the ring (18 in Fig. 1), and the difference between these points was measured. Also, the temperature differences were measured between the bottom of the bed [a thermocouple clamped under the bolt (22)] and the covers of the main cylinder, the windows, and the outside of the cell.

Three different test runs were performed. In the first run, the conical apertures of the cell were closed with covers that were used to press thermocouples against the back

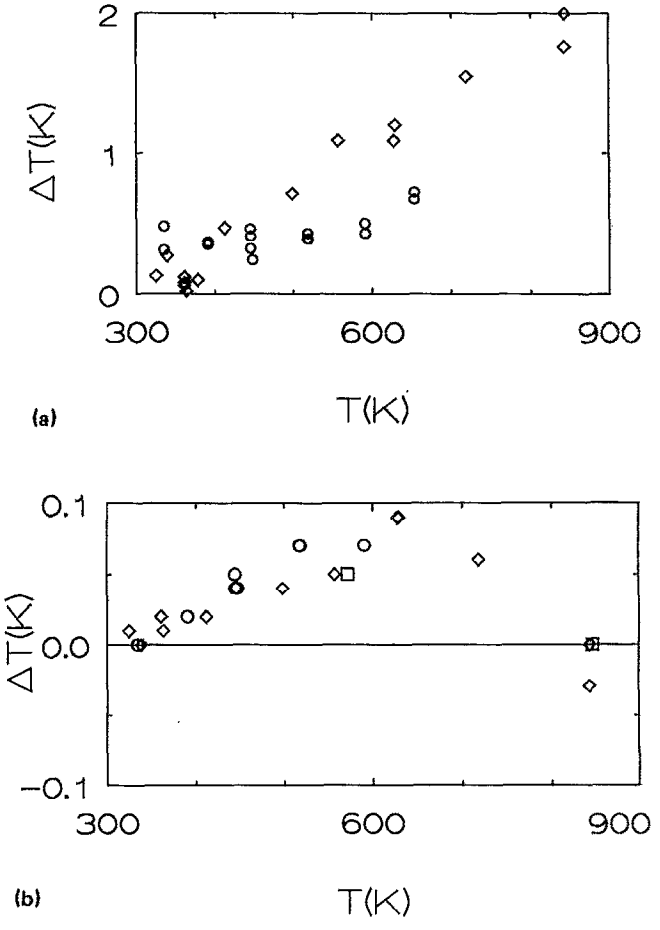

FIG. 4. (a) Temperature between the diamonds minus temperature below the bed (vs temperature between the diamonds). (b) Temperature between the diamonds minus temperature on ring No. 12 vs temperature. In all graphs, circles indicate run 1, diamonds run 2, and squares run 3.

of the diamonds. In the second and third runs, these covers were omitted, because they prevent thermal radiative losses from the diamonds and thus influence the temperature distribution in the vicinity of the sample. In the first run, the cell was heated up to 650 K, while 850 K was reached in the other two runs. Note that the gradients in the cell were measured in steady state, after waiting for 1 day. In Fig. 4(a), the temperature between the diamonds minus the temperature below the bed is plotted. It increased slightly in the first run (indicated by the circles). The offset at 300 K may be caused by an offset in the voltmeter. In the second run (indicated by the diamonds), the difference increases linearly with temperature to a maximum of about 2 K at 850 K. The smaller difference in the first run is probably caused by the fact that the covers on the openings smooth the temperature profile inside the cell. The temperature at the sample minus the temperature at the ring (18) is shown in Fig. 4(b). We see that this difference increases with temperature in all experiments up to about 700 K. It then decreases and at 850 K, it is again nearly zero. This behavior may be due to heat loss from the diamonds through the windows by radiation. We have also attempted to measure the temperature difference between the backs of

the diamonds. In the first run, no difference was observed. In the other runs, no consistent results were obtained, probably because the thermocouple experienced heat transfer to other parts of the cell. From these results, we estimate the temperature variations in the sample space to be smaller than 0.5 K.

The temperature differences between the cell and the covers of the main cylinder and between the cell and the windows were less than 15 and 6 K, respectively. Since the thermal gradients inside the cell are smaller, this suggests that the small heater is very useful in smoothing the gradients inside the cylinder. The temperature difference with the window increased linearly with temperature, while the others increased more at high temperatures. The nonlinearity of the temperature difference hints to radiative or convective transfer and the linear behavior to conductive transfer.

The temperature differences between the main cylinder and the box increased nearly linearly to about 440 K at 850 K. Therefore, the insulating material in the box takes the largest gradients, as it should. The nearly linear behavior suggests that the heat is mainly transferred through conduction and not through convection or radiation.

The change in temperature due to the insertion of the rods that are used to change the pressure have also been measured. At 570 K, the temperature at the diamonds drops 1 K before rising to 0.5 K below the initial value. At the same time, the difference between the diamonds and the ring (18 in Fig. 1) increases from 0.05 K to 0.2 K before dropping to an equilibrium value of 0.15 K. After taking out the rods, the temperatures regain the initial values. At 850 K, the "sample" temperature drops about 2.5 K before equilibrating at 1 K below the initial temperature. The temperature difference between the diamonds and the ring (18) increases from 0.00 to 0.17 K before reaching a value of 0.1 K. Again, after taking out the rods, the temperatures recover the initial values. This shows that pressurizing at high temperatures does not affect the sample temperature seriously.

The long-term temperature stability at 650 K was observed to be better than 0.1 K over a period of 8 h.

After the test of the thermal behavior of the system, two experiments on the behavior under pressure were performed. Pure nitrogen was loaded in a T301 gasket using the existing high-pressure loading vessel. At 37 kbar, quasi-isochoric p-T scans were performed to measure the melting line of nitrogen. The results of two scans are plotted in Fig. 5. At increasing temperature, the pressure increases slightly in the solid phase before it rises steeply following the melting line; subsequently, it increases slightly in the fluid phase. The midpoint of the transition is at 370 K and 37.1 kbar, in very good agreement with the previous results of Ref. 11 (shown as the full curve in Fig. 5). The melting of nitrogen also was observed visually. Heating at a rate of about 5 K/min, the contraction of an interface was observed at about 380 K and 40 kbar, again in agreement with Ref. 11. Note that with the DAC used in Ref. 11, melting of nitrogen could not be observed visually. The advantage of the HTDAC is probably that the maximum heating rate is more than twice as large as that of the other DAC, so that melting proceeds twice as fast.

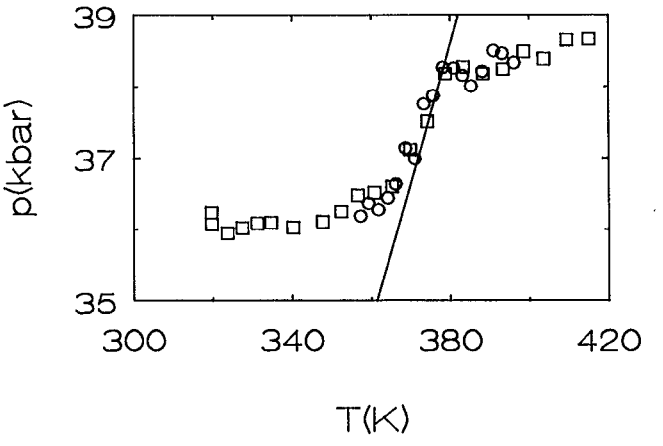

FIG. 5. Quasi-isochoric p-T scan through the melting line of pure nitrogen. Different symbols indicated different scans. The drawn line is the smoothed melting curve of Ref. 11.

We have tried to determine whether the pressure in the cell could be increased at high temperature. At 657 K, it was increased smoothly from 7 to about 12 kbar in 10 steps.[12] During the process, in which the rods were inserted regularly in and taken out of the cell, the temperature did not change by more than 2 K (see also above). The pressure could also be decreased gradually: At 500 K, it was released from 29 to 20 kbar in 4 steps, again without changing the temperature more than 2 K.

It is our experience that the wedge can be left unsupported without a drop in the pressure. After increasing the pressure to 60 kbar at 400 K, the wedge was left unsupported for 1 day, during which no changes in pressure were observed. Furthermore, in a different DAC[13] with a wedge with an angle of 5°, it was observed that at pressures up to 50 kbar, the pressure did not change for periods of days.

Pressures of 50 kbar could be reached easily at 650 K.[14] This should be sufficient to extend the previous measurements on mixtures containing water over a factor of 20 in pressure. This is being attempted currently in our laboratory.[15]

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