Offprinted from the *Transactions of The Faraday Society*.
No. 576, Vol. 66, Part 12, December, 1970

HIGH PRESSURE VESSEL FOR OPTICAL STUDIES IN THE 1-8000 ATM RANGE

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High Pressure Vessel for Optical Studies in the 1-8000 atm range

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Received 10*th June*, 1970

A portable high-pressure vessel is described. It weighs less than 20 kg and can maintain a pressure as high as 8000 atm after being detached from a press or intensifier. Its optical windows (2, 3 or more) make it possible to study the effect of pressure upon light scattering, u.-v., visible and infra-red spectra of substances, their fluorescence etc. Many important technical improvements are outlined.

Spectroscopic and other optical studies of solutions under high pressure are of considerable interest. Pressure perturbs molecular energy levels, and, since such perturbations depend on the character of intra- and inter-molecular forces operating in the liquid, much information about their nature may be gained from studies of such systems. In most cases, it is sufficient to attain pressures of 5000-10 000 atm to induce appreciable changes in the properties of the solutions.

Optical studies under high pressure are greatly facilitated if the pressure vessel, provided with suitable windows, is portable and maintains the pressure developed in it after its detachment from the hydraulic press or intensifier. Such a vessel can be placed in conventional optical instruments for measuring u.-v., visible and i.-r. spectra, fluorescence and phosphorescence, light-scattering, etc. An apparatus fulfilling these conditions has been described in a preliminary note.[1] A detailed description of a slightly modified design and of its operation is given below.

GENERAL DESIGN CONSIDERATIONS

The geometrical configuration of the pressure vessel depends on its particular use and can be varied within wide limits. However, the weight should be minimized so that it is easily portable ; the vessels made in this Institute weigh less than 20 kg.

The four most important parts of such vessels are the pistons, the locking system which maintains the pressure, the windows with their support and the optical cells. For the moderate pressure-range (< 8000 atm) the design can be simple, reliable and convenient to work with. The parts have been standardized and therefore may be used in vessels of different geometry. In all our studies, glycerol was used as the pressure transmitting medium. Its good optical transmission, low compressibility and small tendency to leak out makes it superior to other fluids.

THE MAIN BODY is usually cylindrical. The central axial hole, with pistons and supporting screws placed at *both* ends, forms the main pressurized volume. Such an arrangement facilitates the dismounting of the vessel, which is awkward when it is closed at one end and equipped with only one piston. The increased number of pistons causes no trouble because the reliability of the O-rings is high. For double-beam work, cells with two axial holes have been built, and for light-scattering work with three and five radial holes.

THE PISTONS are O-ring sealed [2] and made either of steel or Nylon. The number of O-rings on the piston depends on the maximum pressure. Each O-ring supports about 2700 atm. At this critical pressure the liquid suddenly leaks through the first ring and fills the volume separating it from the next one. As the pressure is further increased a second leakage occurs at about 5400 atm filling the volume between the first and second O-rings to this pressure and the volume between the second and the third to about 2700 atm. With four O-rings pressures up to 11 000 atm could be securely maintained.

THE PRESSURE-LOCKING SYSTEM is of the same type as described earlier.[1] After mounting the stationary bottom piston, the window pistons, and the sample cell, the vessel is placed in a vertical position and filled with the proper amount of glycerol. The top piston is inserted and its supporting screw, which has a *central bore*, screwed against it. The whole assembly is placed in a hydraulic press, and a steel rod is inserted into the screw bore. When pressure is applied to the protruding rod the top piston is driven down as the pressure increases leaving a space between itself and its supporting screw. After attaining the desired pressure the top screw is screwed tight against the plug. The force on the rod is then relieved and the rod in the screw bore removed. However, the pressure in the vessel is retained by the screws. In fact, it only drops by a few percent due to the yield in the screw.

The cell is now ready to be placed in the optical instrument and the required measurements may be performed. After their completion, the pressure may be increased by repeating the previously described operation, or the vessel may be disassembled by applying again the external force, releasing the screw supporting the piston, which then becomes loose; thereafter carrying out the decompression by a slow release of the external force.

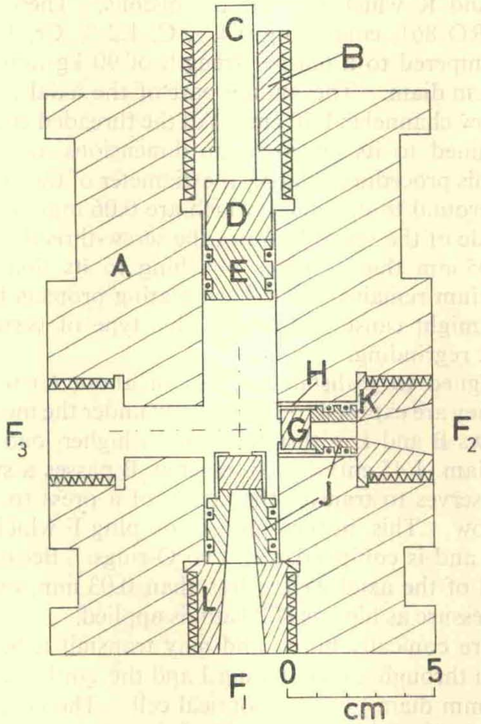

FIG. 1. A high pressure vessel

THE WINDOW SUPPORT is of the conventional unsupported area type.[3] The window pistons are of steel with holes for the light beam and normally provided with only two O-rings. They are supported by screws with tapered holes for the light beam. Previously [1] the windows were either kept in place with water-glass cement, or Poulters method [4] was used to obtain a close fit at low pressures—once the pressure gets high, the windows are leak-proof. In our present design each window G is enclosed in a threaded steel cap H, and is pressed by a plastic gasket against the inner side of the window. In this way the outer side of the window G is pressed against the optically flat surface of the steel piston J even before the high pressure is applied (see fig. 1). This arrangement is extremely convenient.

THE OPTICAL CELL contains the solution to be investigated. Since the cell is immersed in glycerol it must be leak-proof but flexible to allow the compression of the solution as the pressure of the outside liquid rises. Different designs have been tested. The best are: Teflon bellows or cells sealed by pistons with O-rings. The latter are preferred, especially for the light scattering work, because the solution may be maintained dust-free.

TECHNICAL DETAILS

In the studies reported in parts 2 and 3, the high pressure vessel shown in fig. 1 was used. It is provided with three windows, two for a straight-through beam, and the third, conveniently placed in the bottom piston, permitting observation at 90° to the other beam. This design is preferable, as it is more convenient to place a window in the bottom piston than in the wall of the vessel. A thick, cylindrical block A, with an axial hole and a smaller channel perpendicular to it for the light-beam, forms the main body. Both channels have wider ends, which are threaded to take screws B, L and K which support the pistons. These parts are machined out of Bofors steel CRO 861, containing 0.4 % C, 1.2 % Cr, 1.4 % Ni, 1.0 % Mn and 0.2 % Mo and tempered to a tensile strength of 90 kg/mm^2. The main block is 19 cm long and 13 cm diam. The middle part of the axial hole is 2.46 cm diam. while that of the window channel is 1.70 cm. All the threaded ends are 3.60 cm diam.

The body is machined to its approximate dimensions and then prestressed at about 10 000 atm. This procedure enlarges the diameter of the hole by about 0.5 mm. The holes are then reground to diameters which are 0.06 mm larger than the desired dimensions. The inside of the vessel (but not the screw-threads) is then given a hard chromium plating 0.05 mm thick. After polishing to its final dimensions, about 0.03 mm of the chromium remains. The hard plating protects the inner parts from scratches which later might cause jamming. This type of vessel can with care be used for years without regrinding.

Screws K are designed to withstand a load of about 60 tons each when fully screwed in, although they are exposed to 30 tons only under the most severe operational conditions, while screws B and L withstand an even higher load.

Through a hole (diam. 1.45 cm) drilled in screw B passes a steel piston C (diam. 1.40 cm). The latter serves to transfer the action of a press to a tightly fitted steel plunger D located below. This, in turn, presses on plug E which is machined either from steel or Nylon [2] and is equipped with two O-rings. Because the gap between piston D and the wall of the axial well is less than 0.03 mm, even Nylon does not creep into it when a pressure as high as 8000 atm is applied.

Screws K and L are conically bored and may transmit a beam of light 6.5 mm wide which passes then through a hole in plug J and the synthetic sapphire window G (12 mm thick and 15 mm diam.) into the optical cell. The *c*-axis of the sapphire is perpendicular to the optically-flat face to provide the maximum strength to the window, its edges being ground by about ½ mm and thus form conical rims. This reduces markedly chipping of the windows which may occur under pressure. The window, plugs J, D and E are made of Bofors steel ROP 21 (1 % C, 5.5 % Cr, 1.1 % Mo and 0.2 % V) hardened to about 56 Rockwell C. The O-rings are made of nitrile rubber of hardness 70 IHR.

OPTICAL CELLS

The liquid to be investigated is enclosed in a cylindrical Pyrex or quartz cell having an optically flat bottom and two, oppositely placed, optically flat windows. Depending on requirements the windows are 15 mm or 2 mm apart and, if necessary, a quartz spacer may reduce the optical path to about 0.1 mm. A specially designed holder keeps the cell rigidly in the required position.

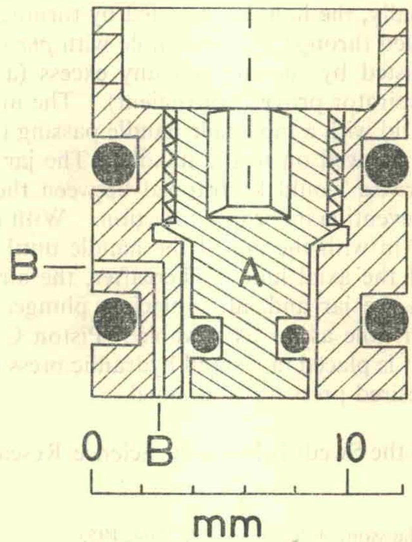

FIG. 2. An O-ring plug for the optical cell

The optical cell, after being filled with the solution, is closed by an O-ring sealed steel plug composed of two parts, as shown in fig. 2, to facilitate opening of the cell. Each part is fitted with O-rings, both their material and hardness being chosen according to the nature of the investigated solution. On placing the outer parts together, some liquid from the cell is first squeezed through a tiny channel, as shown in the figure, into the space between the outer O-rings. At the same time its level rises in the inner hole. Thereafter, the inner part is screwed in and, as soon as its O-ring seals the liquid, further screwing in presses the whole plug slightly up. Thus the solution is tightly sealed in the cell and air bubbles are absent.

The tiny channel is of great importance. In its absence, glycerol may suddenly leak through the outer O-ring and accumulate at high pressure between the O-rings. when the critical pressure is reached. The liquid then bursts the cell during decompression. The channel equalizes the pressure inside the cell and in the space between the O-rings and thus prevents its destruction. Hence, only one O-ring (the outer) is used for sealing, the other serves to provide mechanical guidance. If necessary, two such pistons can be placed, one above the other, for protection of the solution which may be destroyed by its contact with glycerol wetting the cell wall.

ASSEMBLING OF THE HIGH-PRESSURE VESSEL

The following procedure is adopted in assembling the high-pressure vessel. Each side window, enclosed in its holder with plug J screwed in, is inserted into the horizontal well through the appropriate hole (F_2 or F_3). With the aid of a special key the windows are manually positioned so that the O-rings of plugs J enter the narrower part of the well. Thereafter, the holes F_2 and F_3 are plugged by fully turning in screws K.

The optical cell, after being filled with the solution and sealed by its plug, is inserted into its holder. The bottom window in its enclosure H, with the third plug J attached to it, is pressed against the cell holder thus pushing the cell into its proper position. The whole unit, mounted on a special cylindrical vice, is passed through hole F_1 into the narrow part of the axial well and by manual adjustment the correct position of the cell is ascertained. Finally, the hole F_1 is sealed by turning in screw L.

The vessel is now filled through its upper hole with *purum* grade glycerol and the level of the liquid adjusted by sucking out any excess (a specially mounted tube connected to a water aspirator proved convenient). The unit is placed in a vacuum jar which is closed by a lid with a moveable handle passing through its centre, plug E having been previously screwed on to the handle. The jar is evacuated in order to remove air which otherwise would be trapped between the glycerol and the tight-fitting piston thereby preventing its proper insertion. With the air removed, the plug E can easily be pressed in with the aid of the handle until its O-rings are squeezed into the narrow part of the axial hole. Thereafter, the air is allowed to enter, the vessel is removed from the jar and, after placing plunger D in the well, screw B is turned into the upper hole as far as possible. Piston C is now inserted into the bore of screw B, the unit is placed in a small hydraulic press (30 tons) and the content compressed until the desired pressure is attained.

Financial support from the Swedish National Science Research Council is gratefully acknowledged.

[1] S. Malmrud and S. Claesson, *Acta Imeko III*, 1964, 195.
[2] S. Malmrud and G. Andersson, *Rev. Sci. Instr.*, 1962, **33**, 1277.
[3] P. W. Bridgman, *Physics of High Pressure* (Bell and Sons, London, 1958), p. 72.
[4] T. C. Poulter, *Phys. Rev.*, 1930, **35**, 297.

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