Apparatus for Optical Studies to Very High Pressures*

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An apparatus has been developed in two stages which permits optical studies to 200 000 atmospheres pressure. The use of NaCl windows permits studies in the near ultraviolet and in the infrared as well as in the visible. The design of the pressure cells and of a press suitable to fit in a spectrometer are described with essential dimensions. A calibration tested against Bridgman's data to 87 000 atmospheres is given.

EQUIPMENT has been developed which permits the observation of the effect of pressure on optical phenomena at least to 200 000 atmospheres pressure. The apparatus is in two stages, one of which is operable to 60 000 atmospheres while the second is used in the higher range. These are described as Cell I and Cell II below.

Both cells use an alkali halide (normally NaCl) as a pressure transmitting "fluid," and NaCl windows. Although sodium chloride has a relatively low shear strength and is effectively a fluid at very high pressure, it is a very viscous fluid. When fused in a long narrow

hole by the repeated application of 30 000–40 000 atmospheres pressure at both ends, it is not extruded for a very long time even under the action of 60–80 000 atmospheres pressure. Using relatively intense light sources many optical and spectroscopic observations can thus be carried out on a sample at high pressure.

CELL I

The outer steel jacket (B) is AISI 6150 steel hardened to 46-48 Rockwell C (Fig. 1). The inner cell (A) is made from Solar steel hardened to 58–60 Rockwell C and is pressed into (B). The carboloy pistons (C) are grade 883 or 999 jacketed with AISI 4140 hardened to 42-44 Rockwell C. Only the lower piston ($\frac{1}{8}$ in. diam) moves.
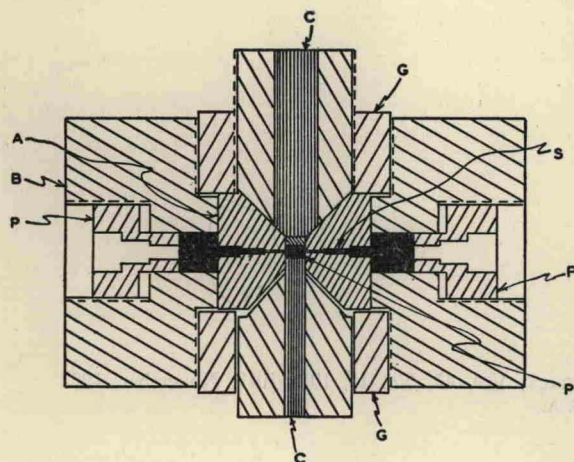
FIG. 1. Cell I—for 60 000 atmos.

The salt windows S consist of three sections in the Solar insert plus an outer section. From the inside a hole $\frac{1}{8}$ in. long 0.028 in. in diam, a hole $\frac{1}{8}$ in. long 0.047 in. diam, and a hole $\frac{3}{32}$ in. long 0.067 in. diam. The outer hole is $\frac{1}{4}$ in. in diam and is filled approximately $\frac{1}{4}$ in. deep. The windows are filled by applying pressure to heated NaCl crystals placed in the outer hole and in the center.

The inner chamber is $\frac{3}{16}$ in. long and is lapped to fit the pistons to 0.0005 in. The holes gradually stretch in service and the inserts must be replaced after 15–30 runs. The pressure is alternately applied in the center and at the outside until the windows become sufficiently clear. This may take as many as half a dozen applications of alternating pressure of about 30 000 atmospheres. The outer plugs P serve to minimize the breakup of the outer edges of the windows. The center NaCl can be removed and the sample inserted, usually in a very thin section between two alkali halide crystals. Thus it is not affected by any extrusion which takes place. The salt pellet is usually 0.040–0.060 in. thick. The spectra obtained are reversible with rising and falling pressure within about 5% on the pressure scale, indicating that friction is not large. Phase transitions which are not accompanied by a large "region of indifference" as described by Bridgman also show this reversibility.

The primary calibration was carried out by using the phase transitions observed by Bridgman[1] in bismuth at 24 700 atmospheres and in tellurium at 43 500 atmospheres. The secondary standard is the shift with pressure of the 2210 cm^{-1} vibration of CN-ion dissolved by fusion in NaCl.[2] This vibration shifts continuously to the "blue" (higher frequencies) with pressure. The data can be fitted by the equation

$$p=0.965\Delta\nu+4\times10^{-3}(\Delta\nu)^2+5.3\times10^{-5}(\Delta\nu)^3, \quad (1)$$

[1] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 425 (1942).
[2] A detailed discussion of pressure effects on the CN$^-$ stretching frequency will be published elsewhere.

where $\Delta\nu$ refers to the change in frequency from the atmospheric pressure value in cm^{-1} and p is the pressure in thousands of atmospheres.

Cell I fails somewhere above 50 000 atmospheres because the moving carboloy piston breaks in compression.

CELL II

Cell II (Fig. 2) utilizes the same principles described for Cell I, plus one further development. The pistons are much larger in diameter with a corresponding change in insert size, window holes, etc. Typical dimensions are summarized in Table I. The pistons are tapered with a flat section $\frac{3}{32}$ in. in diam in the center. (This is the smallest flat conveniently operable in our experiments.) When the pressure is applied to the movable piston the center is compressed by a greater percentage than the taper. This results in a pressure gradient from the edge of the flat to the outside edge of the piston. The greater the taper, the higher the gradient, but also the higher the tendency to extrude from the flat section. After trying a wide variety of tapers and combinations of tapers, we found that a single taper of 6° on each piston was the most advantageous. The tapered piston accomplishes several objectives. The very high pressure is only on the center of the piston which does not break because of the principle of "massive support" mentioned by Bridgman. The salt also supports the piston along the taper. The salt from the flat to the outside under a continuously decreasing pressure acts as a series of "cells within a cell" and minimizes extrusion, permitting a pellet of useful thickness in the center. The average applied pressure and the drop in pressure at the outside of the piston is such that the windows have negligible tendency to extrude.

The sample is inserted in a thick slice in the center of the flat portion and perpendicular to the light path.

The pressure obtained is a distinct function of the thickness of the central flat portion (t_C) as well as of the average pressure across the piston (p_A). The pressure was calibrated by using the CN$^-$ stretching frequencies obtained on Cell I and as upper points the phase transitions rated by Bridgman[3] on AgBr at
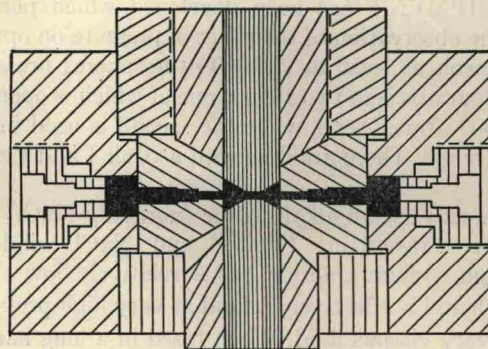

FIG. 2. Cell II—operated to 200 000 atmos.

[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1945).

83 200 atmospheres and AgCl at 87 100 atmospheres. These were observed by following the cut-off of light with recrystallization at the transition both with rising and descending pressure. These points were noted with various sample thicknesses. The results were correlated with observed CN^- shifts at the same thicknesses, and Eq. (1) was developed. All extensions to pressures above 100 000 atmospheres were by means of this relationship and thus involved a varying amount of extrapolation. We have made numerous measurements to 150 000 atmospheres and several to considerably higher pressures. With a sample thickness of 0.0046 in. using the one-half inch pistons we obtained 201 000 atmospheres (with $p_A = 52\,800$ atmos). We have fitted our data empirically with the following relationships:

For the $\frac{3}{8}$ in. diameter piston,

$$p_C = p_A \left[1 + \frac{32.4}{p_A{}^{0.25} t_C{}^{1.25}} \right], \qquad (2)$$

for the $\frac{1}{2}$-in. diameter piston,

$$p_C = p_A \left[1 + \frac{51.8}{p_A{}^{0.25} t_C{}^{1.25}} \right]. \qquad (3)$$

Here p_C is the pressure on the center flat and p_A is the average pressure on the piston, both in thousands of atmospheres, while t_C is the thickness in the center in thousandths of an inch (i.e., for a thickness of 0.009 in., $t_C = 9$) measured at atmospheric pressure. This is obtained by micrometering each piston and then the assembled apparatus after the salt and sample are fused in, then taking the difference. Particularly with old inserts there is some extrusion and t_C at the end
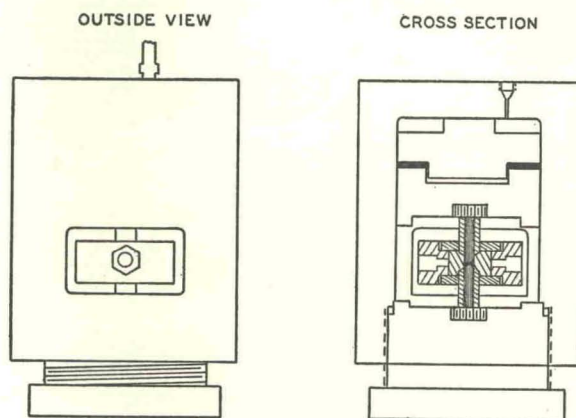

OUTSIDE VIEW   **CROSS SECTION**

Fig. 3. Press.

of the run is slightly different than the initial t_C. (It is essential to micrometer both the assembly and individual pistons at the end as there is measurable shortening of the pistons.) Where t_C varied appreciably from the initial to the final value, it was assumed that the effective t_C varied linearly with p_A, reaching its final value at the highest p_A. Equations (2) and (3) have been tested for values of t_C ranging from 4–15 (0.004–0.015 in.).

The pressures are necessarily less accurate in Cell II, so it is desirable to make all studies in both cells allowing overlap for continuous calibration. It is difficult to estimate exactly the accuracy of the pressure determination. The transitions of the silver halides were reproducible to ±1000 atmospheres. Equations (2) and (3) reproduced a large number of experimental points with the largest deviation in t_C being 0.1 (0.0001 in.) as long as p_C was greater than 50 (50 000 atmospheres).

Figure 3 shows the press constructed for this work. The dimensions can, of course, be varied, but we used a body of AISI 6150 hardened to 45-46 Rockwell C 6 in. o.d. and $4\frac{1}{2}$ in. i.d. The windows are 2 in.×$2\frac{1}{2}$ in. It is necessary to back the pistons with carboloy blocks 1 in. in diam and 1 in. thick. The press is portable and can be inserted at the normal sample point of many spectrometers with minor modifications of the optics.

A wide scope of problems is opened for study by this apparatus. We are measuring electronic and vibrational spectra, absorption edges, luminescent spectra and decay, photoconductivity, and photolysis.

ACKNOWLEDGMENT

TABLE I.[a]

		Cell I (in.)		Cell II (in.)
Piston diameter		$\frac{1}{8}$	$\frac{3}{8}$	$\frac{1}{2}$
Jacket diameter (B)		$3\frac{5}{16}$	$3\frac{5}{16}$	$3\frac{1}{2}$
Cell diameter (A)		1	$1\frac{1}{2}$	$1\frac{7}{8}$
Window holes				
(1)	L	0.125	0.188	0.125
	D	0.028	0.035	0.037
(2)	L	0.125	0.125	0.188
	D	0.047	0.052	0.052
(3)	L	0.188	0.250	0.188
	D	0.067	0.082	0.082
(4)	L	...	...	0.188
	D	...	...	0.100
Diameter of flat		0.125	0.93	0.093
Taper			6°	6°

[a] Note: Holes (1), (2), (3), (4) are numbered from the inside of the insert (A) to the outside.