The minimum wavelength or wavenumber interval which the monochromator can resolve is expressed by the spectral slit width, which can be calculated from the following equation[3]

$$\Delta\tilde{\nu}_s = \tilde{\nu}^2 \frac{d \cos\alpha}{2n} \frac{s}{f} + F(s) \frac{\tilde{\nu}}{Mn}, \quad (2)$$

where

$\tilde{\nu}$ = wavenumber, cm^{-1}
$\Delta\tilde{\nu}_s$ = spectral slit width, cm^{-1}
d = grating constant, distance between successive lines, cm
s = slit aperture, cm
f = focal length, cm
M = total number of lines on the grating

and

$F(s)$ = slit width function.

The exact nature of $F(s)$ is in doubt; as a first approximation it is assumed to be linearly depending on the slit width, having values of 0.9–0.5 for narrow to wide slit widths, respectively. The first term in the equation is called the slit-limiting term, and the second the diffraction-limiting term; the slit term is much larger than the diffraction term, from two to 20 times greater, depending on the wavenumber.

The energy which passes through the exit slit and falls on the detector is proportional to the slit height and the square of the slit width. Therefore, a wider slit width gives a stronger signal to operate the mechanical servo assembly, but it also causes a poorer resolution.

Since the focal length of the monochromator was extended from 35 to 40 cm, a stronger light source was required. The radiant power falling on the detector[3] is given by the equation

$$P_\nu = \frac{B_\nu h s^2 A T_\nu \nu^2}{16\pi f^3 c (d\theta/d\lambda)}, \quad (3)$$

where

P_ν = the radiant power falling on the detector,
B_ν = the brightness
h,s = slit height and width, respectively
A = area of collimator optical surface
f = the focal length
c = the velocity of light
$(d\theta/d\lambda)$ = the angular dispersion of the grating
ν = frequency, cps
T_ν = the efficiency of the various monochromator optical parts.

According to this equation, the radiant power on the detector is reduced to 34.3% of the original value. In order to make up this loss, the voltage across the source element was increased, with a corresponding reduction in life expectancy.

A PEN-RAY argon–mercury quartz lamp, manufactured by Ultra-Violet Products, Inc., San Gabriel, Calif., with a special transformer, was used as the light source for the optical alignment of the monochromator. The lamp, 6.5-mm diam × 5.08-cm long emitting tube, provides seven discrete spectral lines at 2537 Å, 3125 Å, 3650 Å, 4358 Å, 5461 Å, and 5770 Å. When the lamp replaces the light source of the spectrophotometer, the image of the lamp can be observed in the center part of the grating, and after dispersion a spectrum of different colors appears. The green light, 5461 Å, is used to align all optical components after the grating. When all components are in the correct positions and angles, the green beam is focused on the crystal surface of the detector.

B. The Pressuring System

Figure 2 is a schematic of the pressure producing apparatus and consists of two parts. The low pressure part is mounted on a relay rack panel and consists of a pump, oil reservoir, a pressure gauge and the appropriate valves.

The second part of the apparatus, a pressure intensifier shown in Fig. 3, multiplies the low pressure by a factor of approximately 16. The design is similar to one appearing in the literature by Fishman and Drickamer.[7] The main body of the intensifier is constructed of AISI 4340 steel hardened to 50 Rockwell C. The piston arrangement is constructed of Sagamore tool steel hardened to 55 Rockwell C. Both the high and low pressure ends of the piston are sealed by the Bridgman unsupported-area principle,[8] and the seal rings are constructed of Teflon. The low pressure is connected to the ir cell by Harwood ⅛-in. tubing and

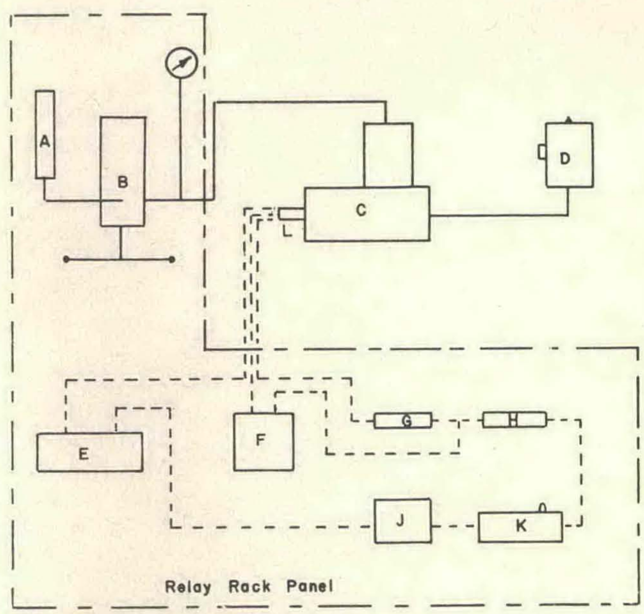

FIG. 2. Pressuring and measurement system. (A) Oil reservoir; (B) Aminco 0–15000 psi pump; (C) 16–1 pressure intensifier; (D) I–R cell; (E) Kepco model ABC power supply; (F) L & N model 9834–1 null detector; (G) 2100 Ω resistor; (H) 2000 Ω resistor; (J) L & N model 4776 resistance box; (K) L & N model 4258 slidewire; (L) strain gauge pressure transducer.

fittings. A pressure transducer[9] is mounted in the intensifier; between the transducer and the intensifier is a metal-to-metal conical seal. A short plug with both ends machined to 59° is fitted into 60° receptacles between the two pieces. The intensifier has been pressure tested to approximately 10 000 atm.

C. The 0–1500 Atm Cell

Figure 4 shows the 0–1500-atm variable path ir cell, which was constructed of type 303 stainless steel. Windows for the cell are either Irtran 1 or 2 obtained from Eastman Kodak Company. Three plugs were made for the cell; by choosing the proper two, the path length can be approximately 0, $\frac{1}{4}$, or $\frac{1}{2}$ in. Fine adjustment of the path length is made by varying the length of the retaining rings. The two plugs are held in place with six stainless steel cap screws each, and the pressure seal is obtained with Viton O-rings. This cell is equipped with Harwood $\frac{1}{8}$-in. tubing fittings. Cells of the two plug type, capable of withstanding up to 12 000 atm, have been built by other investigators.[7]

D. The 1000–10 000 Atm Cell

A high-pressure cell was designed to operate under various pressures up to 10 000 atm, and consists of four major parts: body, plug, seal rings, and windows.

The cell body shown in Fig. 5 is a 4-in. cubical block, made of SAE 4140 annealed steel and heat treated to the hardness 48/52 Rockwell C. The beam of light path through the cell is 0.203 in. and the cell holds approximately 0.0205 cm^3 of sample. The surface which supports and seals the window was ground and lapped to approximately 4–6 μ flat.

Because of the irregular configurations of the cell body, an exact stress analysis is quite complicated. However, an approximate calculation was made, and indicated that the maximum shear stress would be approximately 37 000 psi and the maximum compressive stress approximately 155 000 psi, compared to a maximum allowable shear and compressive stress for SAE 4140 annealed steel after heat treatment of 140 000 psi and 200 000 psi, respectively.

The plug, made from graph-air tool steel which has the least distortion during heat treatment, was heat treated to 58–62 Rockwell C hardness. The plug has a 1.456-in. major diam and 16 threads/in. (American National), and is 2.476 in. long. A 45° slope in the shoulder of the plug provides a free space for the deformation of the steel ring under high pressures. The end which supports the window was ground and lapped to 4–6 μ flat.

A two-stage technique is used to seal the plug based on Bridgman's[8] pipe connection, and includes two different steel rings and one O-ring.

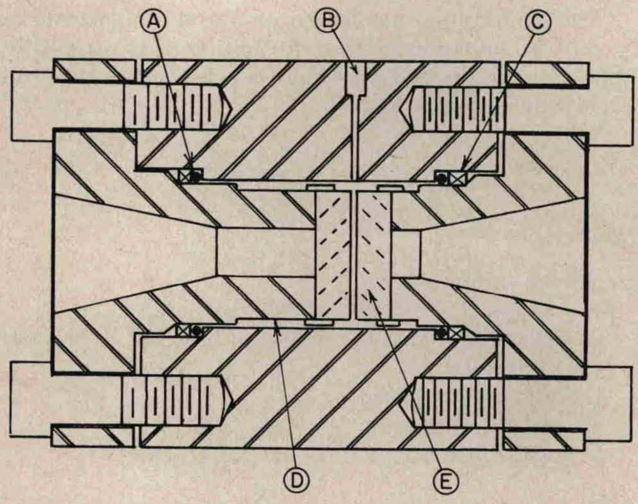

FIG. 4. 0–1500 atm cell. (A) Viton O-rings; (B) Harwood Series 2M fitting; (C) adjustable retaining rings; (D) variable plug dimension; (E) Irtran window.

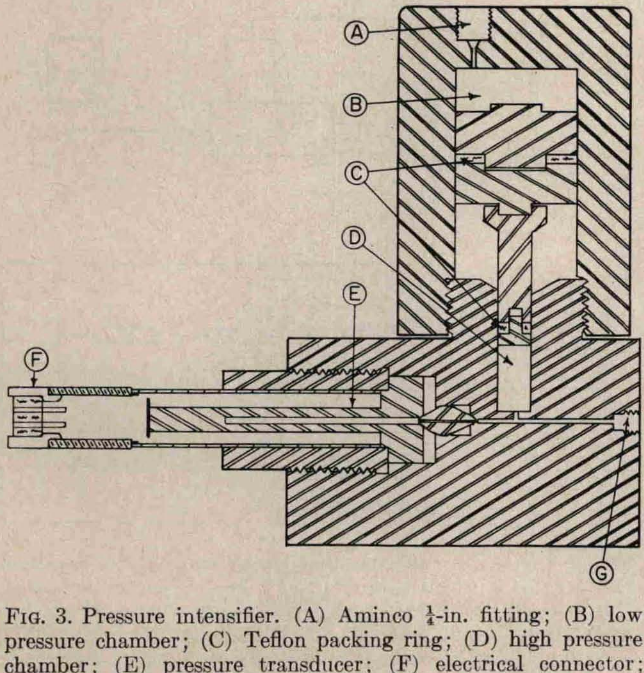

FIG. 3. Pressure intensifier. (A) Aminco $\frac{1}{4}$-in. fitting; (B) low pressure chamber; (C) Teflon packing ring; (D) high pressure chamber; (E) pressure transducer; (F) electrical connector; (G) Harwood series 2M fitting.

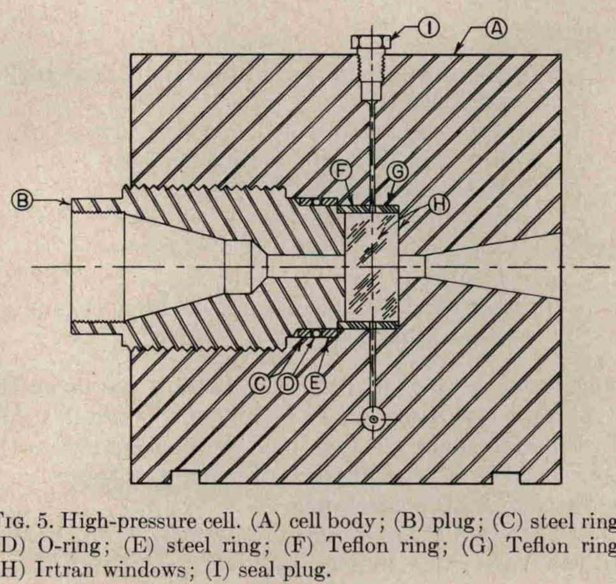

FIG. 5. High-pressure cell. (A) cell body; (B) plug; (C) steel ring; (D) O-ring; (E) steel ring; (F) Teflon ring; (G) Teflon ring; (H) Irtran windows; (I) seal plug.