Construction of a diamond anvil based spectroscopy system for investigation of aromatic interactions under high pressure

Background

Despite the fact that the currently used techniques to investigate super high pressure systems have existed in essentially their modern form since the mid 70s[1][2], this field nevertheless remains quite neglected. A lot of this comes from the relative difficulty of creating high pressures as compared to high temperatures, which are considered an attractive alternative.

Though it is possible to create very high pressures in a transient manner by intersecting several intense sound pulses or by quickly evaporating a liquid medium by way of strong laser pulses, the very short (< 1 ms) time scale of these pressure wave precludes long term studies, and can impede some spectroscopic methods.[3]

Thus, the tool of choice for most scientists investigating these phenomena is the anvil cell, a device which exploits mechanical advantage by employing tapering blocks, and applying pressure to the large end. Specifically, *diamond* anvil cells (DACs) are preferred. These are anvil cells where the anvils are diamonds. As an anvil cell material, diamond is preferred in part because it is very strong and deforms only very slightly under very high pressure, but mostly because it is transparent throughout the entire visible spectrum, and briefly into both the ultraviolet and infrared.[4]

Even if real time spectrometric access to the sample is not needed for the investigation at hand, DACs are excellent because they allow for the pressure inside the cell to be tracked easily. While there is theoretically a direct, mechanical-advantage-type relation between pressure applied to the anvil cell and pressure inside it, non-idealities in the system (primarily the deformation of the materials used to construct the cell) mean that the mechanical advantage cannot be used with applied pressure to accurately predict internal pressure. Instead, several other methods are used, the most common of which is the red shifting of the ruby R1 fluorescence line.[5] R1 red shift is ideal because the red shift of the line can be related to the pressure on the crystal via a simple and empirical, but very well tested, formula. Additionally, R1 shifts have been used to determine pressure accurately up to pressures as high as 156 GPa![6]

Components and Setups

The anvil cell

The anvil cell employed was a Diacell© μScopeDAC-RT(G), manufactured by easyLab of Reading, United Kingdom. In this cell, the sample is held in a cavity drilled

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[1] J.D. Barnett, S. Block, and G.J. Piermarini. "An Optical Fluorescence System for Quantitative Measurement in the Diamond-Anvil Cell", *Rev. Sci. Instrum.*44 1 (1973) doi:10.1063/1.168593

[2] Vincenzo Shettino et. Al., "Chemical Reactions at Very High Pressure", *Advances in Chemical Physics* v. 131 2005 pg 111.

[3] H.K. Park, D. Kim, C.P. Grigoropoulos, and A.C. Tam, "Pressure generation and measurement in the rapid vaporization of water on a pulsed-laser-heated-surface". *Journal of Applied Physics* 80 (7), 1 October 1996 pp 4072-4081

[4] Schettino

[5] Ibid.

[6] J.H. Eggert, K.A. Goettel, and I.F. Silvera, "Ruby at high pressure. I. Optical line shifts to 156 GPa", *Phys. Rev. B* 40, 5724-5732 (1989)

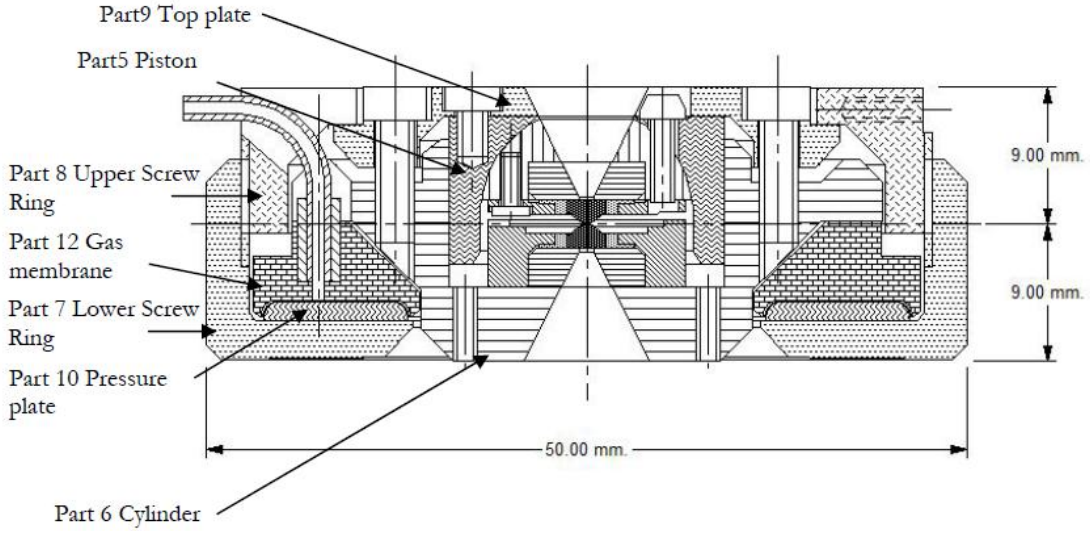
into a metal gasket, which is then pressed between the two diamond anvils. One of the anvils, attached to the cell body, is held stationary during operation. The other anvil, attached to the cell piston, is driven towards the sample and stationary anvil by way of a thin metal membrane, which is filled with pressurized gas. As the pressure of the gas in the membrane increases, the membrane displaces slightly but with a lot of force, driving the anvil.

With this system, applied pressure can controlled within fractions of a bar of applied pressure, which translates to hundreds of megapascals of pressure inside the sample cavity. While this may not seem very precise, the maximum internal pressure (as recommended by the manufacturer) is 50 GPa; therefore, pressures can be found within a fraction of a percent. This aids not only in precision, but also in repeatability. This contrasts with the other possible method of driving the cell, whereby the piston (and hence the anvil) is driven towards the cell body by way of 4 M3 screws. While the screws are actually capable of driving the cell to higher pressures than the gas membrane (which is damaged if the pressure gets too high), this method is far less precise, due both to the difficulty of hand-tightening screws to great precision, and also due to slight deformations of the screws themselves.

Optical access to the cell is provided through the anvils themselves, which are high grade diamonds. The aperture is approximately 1mm in diameter, with a numerical aperture of 0.54. While this is very useful for allowing access to input sources, allowing multiple light sources to be used simultaneously. This is useful, for example, for performing coherent anti-Stokes Raman (CARS) spectroscopy.

Please note that the part numbers on the below diagram are those assigned by easyLab and are not referenced elsewhere in this paper.

Figure 1: A diagram of the DAC cross section[7]



[7] Diacell μScopeDAC-RT(G) User Guide, Issue 1.2, October 2008 (P00390). © easyLab Technologies Limited, December 2006. Page 9 (Figure 2)

The spectrometer

The spectrometer I used was an Avantes AvaSpec USB 2.0 4 channel spectrometer (AVS-DESKTOP-USB2), which actually consisted of four individual Czerny-Turner monochromators, with ranges of 320-469 nm, 460-589 nm, 580-686 nm, and 659-750 nm respectively. This gives the entire spectrometer an operating range of 320-750 nm, reaching across the entire visible spectrum and into the near ultraviolet. The spectrometer had a resolution of roughly 0.05 nm. Light was coupled into the device via optical fibers, and the device was controlled via proprietary Avantes AvaSoft 7.4 software.

The argon ion laser

The argon ion laser used was a 50 mW output continuous wave argon ion laser manufactured by MWK Industries, with a primary peak at 488 nm.

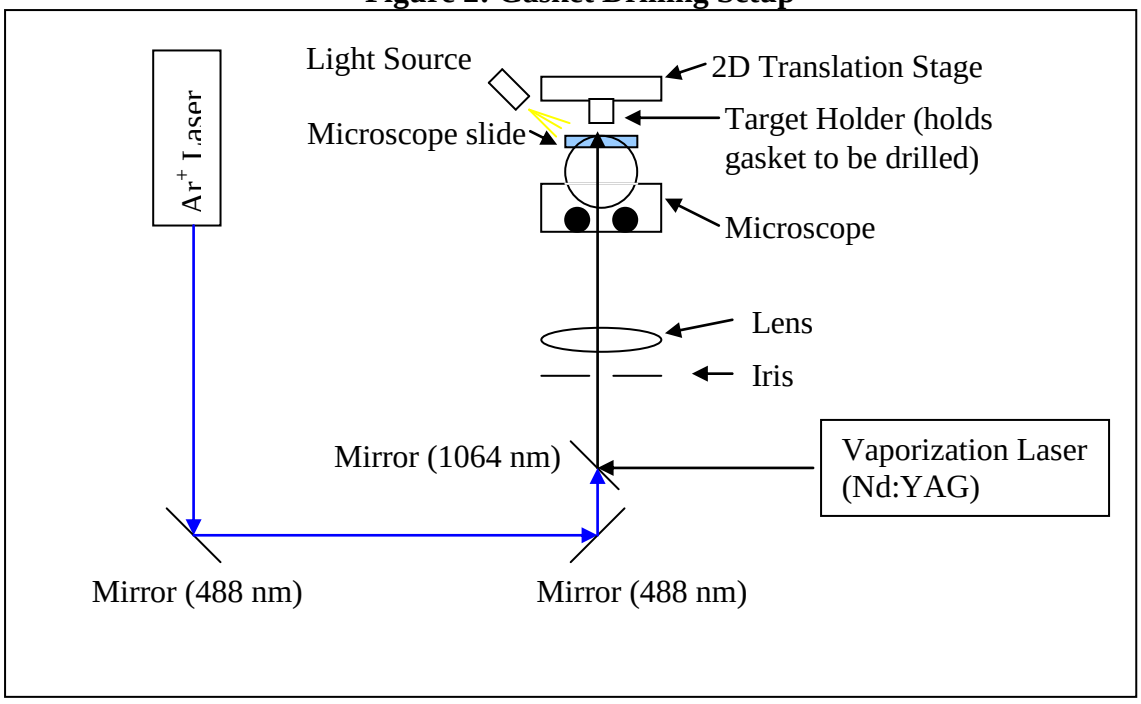
The vaporization laser

Vaporization was conducted using a [laser company] produced neodymium doped yttrium-aluminum-garnet (Nd:YAG) solid state laser Q-switched pulse laser. The laser was pumped by a [] flashlamp operating at 20 Hz. Though the laser was capable of operating with a variable Q-switching time, all hole-drilling operations conducted in the course of this investigation were done with a 280μs delay.

Setup

The spectrometry set up actually consisted of two separate systems, built in parallel and sharing some components. The first is a system for drilling small holes through metal gaskets. As noted above, gaskets used in operation of the diamond anvil cell cannot be purchased pre-drilled, but must instead have holes created after preindentation. This task, this creation of holes with diameters between 75-300μm located with precision of tens of microns, is a nontrivial one. A diagram of this portion of the set up is presented below.

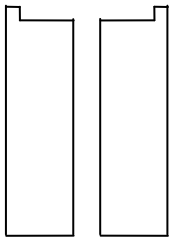
Figure 2: Gasket Drilling Setup



Following the beam line from the vaporization laser through to the target, the first thing encountered is a 1064 nm mirror. As the laser is reflected off of this mirror, the blue Ar^+ laser is brought in from behind, and the two made collinear. The lasers then travel through an adjustable iris. Behind the iris, the beams go through a glass lens that focuses the vaporization laser down to power densities high enough to vaporize the metal of the gasket.

The gasket itself is held by a target holder consisting of an aluminum cylinder with an M4-tapped through-hole drilled, and a shallow (~200 μm deep) depression with a diameter of precisely 1 cm. The gasket is held in the depression, while the through-hole allows the target holder to be affixed to some support via a simple screw. In this case, the holder was affixed to a two dimensional translation stage, allowing the position of the gasket to be adjusted in the *x* and *y* directions, if *z* is taken to be directly along the path of the lasers.

Figure 3: Transverse Section of Target Holder



Between the lens and the gasket lies a glass microscope slide set at 45 °to the vertical. When the gasket is illuminated with a bright light source, this slide reflects an image of the gasket into the microscope, allowing the scope to be used in aiming the vaporization laser. Since the slide is made of thin glass, though, it allows the laser to go through with minimal attenuation.

The spectrometry set up is laid out directly alongside the drilling system, and the two share the Ar^+ laser that is used for aiming the vaporization laser, and for exciting fluorescence during spectrometry. Though the DAC's aperture allows the shining of multiple lasers into the sample chamber simultaneously, space constraints prevent simultaneous input of both laser light for fluorescence and white light (coupled from a halogen light source via optical fiber) for absorption. Thus, the system was operated in two distinct configurations: that in Figure 4, used for fluorescence, and that in Figure 5, used for absorption. These configurations differ only in the source of light, which is a blue argon ion laser focused through a lens onto the sample in the one case, and a halogen white light source coupled through an optical fiber placed adjacent to the anvil face in the other. All other details are the same between the two.

In either case, the DAC itself is held in a rotatable and translatable mount consisting of a ThorLabs 2" Kinematic Optics Mount mounted on a Thorlabs XZ 12.5mm Dovetail Translation Stage. This allowed the DAC to be easily translated and rotated to optimize signal through it. Initial designs had only a translational stage, but experience showed that rotational alignment could have a substantial effect on collected signal.

The DAC's mount is then attached to an aluminum base plate, which is affixed to a bracket holding the collimation tube. The tube contains a pair of matched lenses to collect as much light as possible from the DAC's output, and couple it into an optical fiber connected to the spectrometer.

As well as being mounted in a movable stage, the DAC is connected via a thing metal gas line to a Gas Membrane (GM) Controller, provided by easyLab. This controller is in turn connected to a high pressure regulator attached to a tank of nitrogen gas at ~2000 psi.

Figure 4: Setup for fluorescence

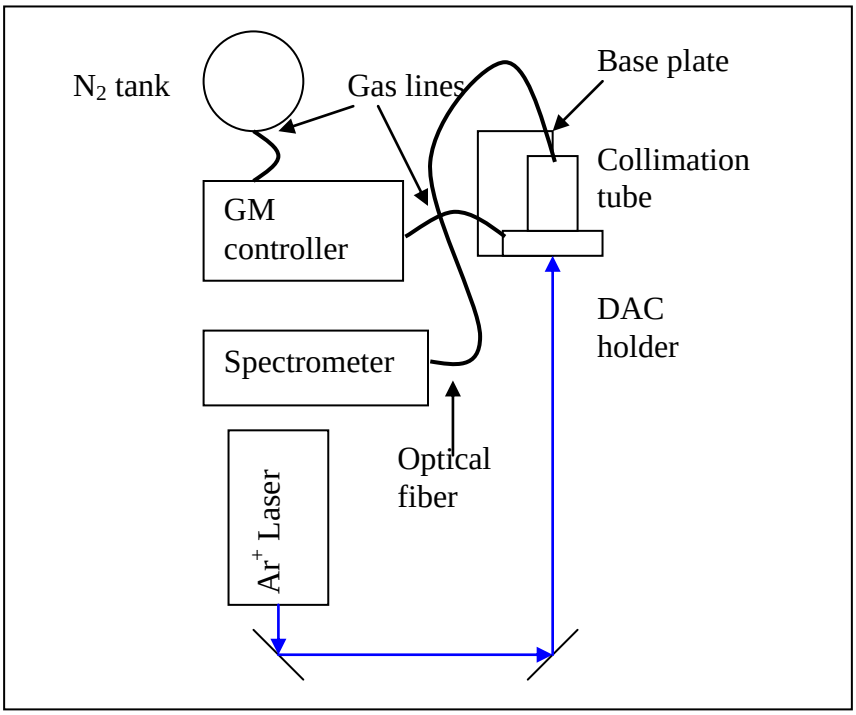
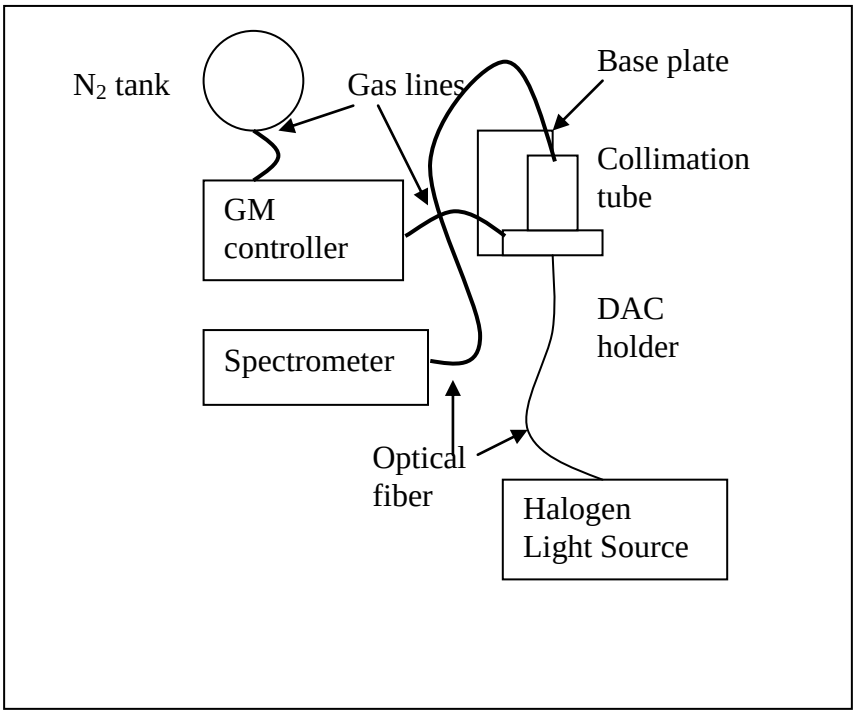


Figure 5: Setup for absorption



HIgh Pressure Investigations

easyLab recommends that the DAC be brought up to high pressures in stages over several pressure runs, checking and adjusting alignment at each one. This is because the alignment of the anvils tends to shift as the diamonds are driven into their tungsten carbide support plates, until they find their final high pressure position. Running the cell with the anvils in anything less than perfectly parallel alignment can cause damage to the anvils or the support plates due to uneven distribution of forces across the item in question.

After assembling the high pressure spectrometry system, I proceeded to bring the DAC up to pressure in several steps. This was done slowly, in steps of ~3 bar applied, though the amount varied from point to point. Internal pressure at all points was measured by red shift of the R1 fluorescence line of several small ruby crystals that had been placed in the sample chamber for the purpose.

For each run, I first selected an unused metal gasket of the type provided by easyLab. These gaskets were 1.0 cm in diameter by 0.25 mm thick, laser cut from rolled 310 stainless steel. This gasket was then preindented by placing it inside the DAC and applying pressure via the clamping screws. The clamping screws were screwed ¼ turn, providing a notional traverse of 0.125 mm on the 0.50 mm pitched M3 screws used.

After preindenting, the gasket is removed from the DAC and a hole drilled through it using the above described hole-drilling system. Vaporization laser power incident to the gasket is approximately 70 mW.

After a hole was drilled in the gasket, it was placed atop the DAC's body-side anvil, and a few grains of ruby powder were placed inside the sample chamber using a fine wire held in a hemostat. A drop of spectroscopy-grade benzene was then placed on the gasket, and the DAC closed and the clamping screws screwed until tightness. The cell was then placed in a fume hood for 15 minutes to allow excess benzene to evaporate.

The cell proper was then placed inside the gas membrane collar, and the gas membrane support collar was tightened, first by hand, and then using a vise and a monkey wrench. The cell was then placed in the DAC mount of the spectroscopy system described above, and allowed to equilibrate for 24 hours. After the equilibration period, pressure was applied via the gas-driving mechanism described above in increments of approximate 3 bar. After each pressure increase, the system was permitted to equilibrate for 30 minutes, and the internal pressure was measured via ruby fluorescence redshift before increasing the pressure once more. Figure X before contains several sample ruby fluorescence spectra, and Figure X contains a plot of internal pressure versus pressure applied for the run which achieved the highest pressure during the investigation period.

A linear best-fit curve applied to the data in Figure 7 between 18 bar applied pressure and 76 bar applied pressure yields a slope of 4850.6. Because the relationship between applied and internal pressure is quite linear within that region, and we know the slope and offset of this line, specific internal pressures can be achieved with both precision and accuracy.

Figure 6: Several Ruby Fluorscence Spectra

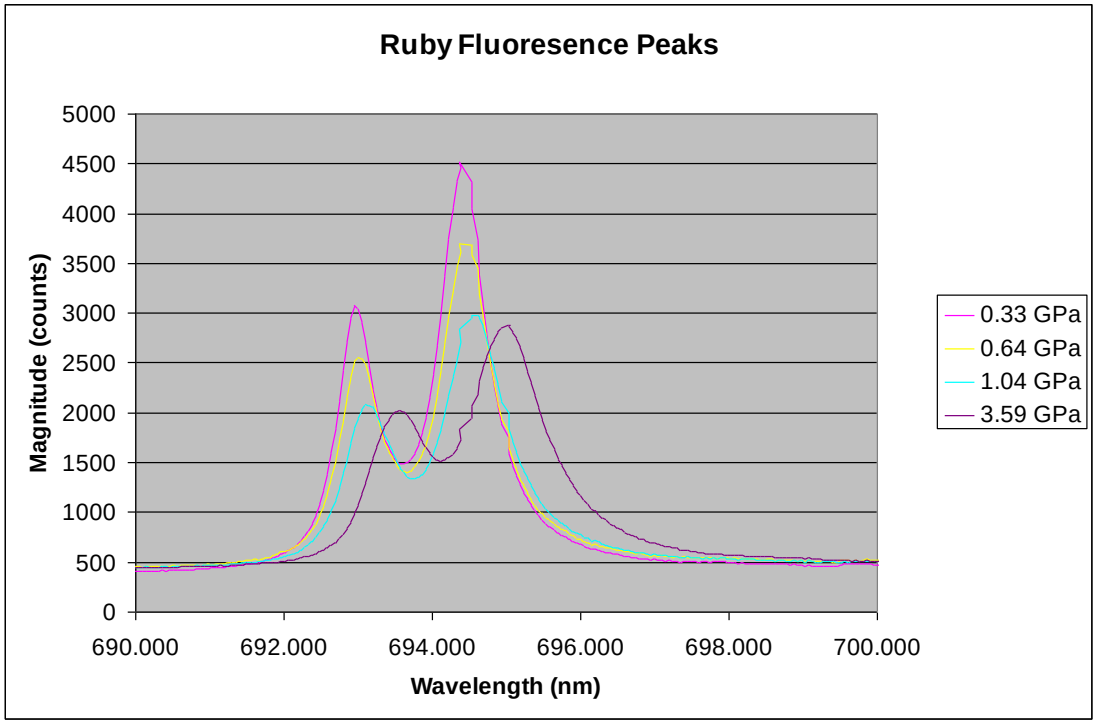
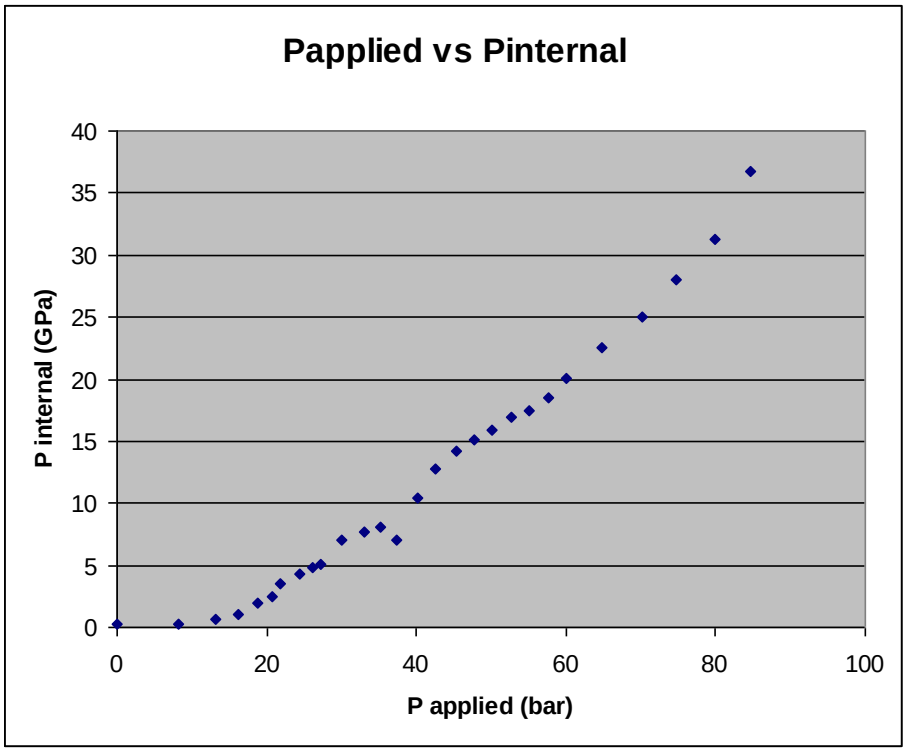


Figure 7: Internal vs applied pressure



Pressure runs often ended when the sample hole closed due to deformation of the gasket metal. After each run, the gasket was removed and stored, and the entire cell checked for damage before the diamonds were realigned. Generally, no realignment was necessary.

Conclusions

As the project was primarily one of construction and engineering, and not of investigative research, no conclusions may be drawn in the classic sense. Nevertheless, conclusions may be drawn in a sense by considering the work done in having constructed a versatile system for conducting high pressure chemical and physical investigations, and in thoroughly testing it.

The ideal method for performing many of the tasks involved was discovered. Among these tasks are preindenting the gasket, drilling the sample hole, loading the sample chamber, tightening the gas membrane support collar, and allowing the DAC to equilibrate after increasing pressure. Though little science *per se* was accomplished this summer, the system is now ready for use in any of a wide array of investigations.