

the force necessary to balance the pressure gradient at the periphery of the piston faces.

The corrections on central sample pressure with reference to the pressure calculated from force and initial piston area are approximately as follows:

Due to pressure gradient at periphery	+3%
Due to stainless steel ring	-2%
Due to elastic distortion of pistons	+1%

The net of these corrections appears to be within the uncertainty of pressure due to lack of precise knowledge of pressure distribution in the sample, so no correction is made. Near the limit of strength of the pistons, large plastic deformations can occur, resulting in increases of piston area by as much as 20 percent. The piston diameter must be measured after each run when in the region of flow. At very low pressures the correction due to the stainless ring can be much larger than 2 percent, and suitable precautions must be taken.

In assembling the pistons, sample, foil, and stainless ring, a split jig is used to insure alignment of all parts. This jig is removed only after several kilobars of pressure have been applied to the sample. From this point on there is no connecting member between the pistons save the sample and ring. There is thus no possibility that the force of the press can be borne by anything except the sample and ring.

#### SAMPLE PREPARATION

The sample is introduced in powder form. Platinum-10% rhodium foil .001" thick is placed between the sample and the pistons, to prevent reaction with the pistons and to facilitate removal of the sample. At temperatures above 500°C, Molykote ( $\text{MoS}_2$ ) is applied to the piston faces to prevent adhesion of the foil. A stainless steel ring is used around the periphery of the piston faces to retain the sample and volatiles and to provide a thicker specimen. The part of this ring between the piston faces is .010" wide and .005" thick. The geometry of a typical ring and sample assembly at low pressure is shown in figure 6. At high pressure, of course, the ring is squeezed down and partially extruded.

If the initial amount of the sample is not too great to fill the void, then the platinum-rhodium foils and the stainless ring are in direct contact, and the pressure deforms them, making a metal-to-metal seal. This was initially thought to be necessary to retain water vapor, but subsequent experience has shown that it is not usually needed.

At moderate to high pressures, the amount of sample present is not critical. An excess of sample can be added, provided it is not so much in excess that it results in a blow-out of the stainless steel rings. In practice, this means that the sample is ladled in with a spatula so that it forms a shallow rounded pile above the ring. The upper platinum foil is emplaced, the upper piston put in, and the assembly placed in the press. We are unable to discover any difference in results correlated with initial amount of sample, so long as the stainless ring remains in position. With excess sample, some is extruded past the stainless ring, forming an annular sheet perhaps .001" thick. Diffusion of water

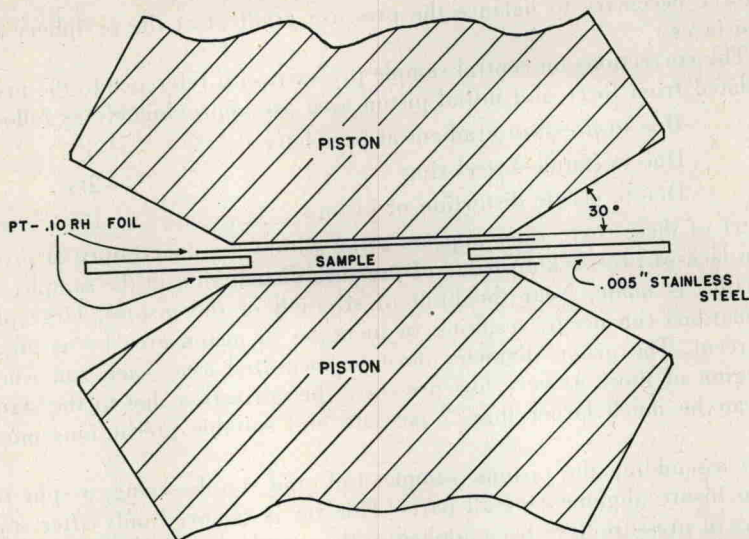


Fig. 6. Exploded assembly showing stainless ring, platinum foil, and sample geometry.

vapor through this extruded material is apparently so slow that it does not interfere with our experiments.

The sample comes out as a lenticular wafer .004"-.015" thick, weighing 1-10 milligrams. It is usually hard and coherent. Under the microscope its crystalline nature is usually evident. Grain size is usually 1-10 microns, so that some optical properties can be determined microscopically. Moderately good X-ray patterns can usually be obtained on a Norelco recording X-ray spectrometer. These X-ray determinations provide the easiest and most unequivocal means of identifying the crystalline phases present in the sample. It has been found that grinding the sample in a mortar before X-raying results in general in a better pattern. This is presumably due to the development of preferred orientation due to the shear stress and/or strain present in the sample under pressure.

#### PROCEDURE

Successful use of this apparatus requires appropriate quenching to preserve the sample in the crystal phase which it had attained at stabilized temperature and pressure. Quenching is normally done by swinging the furnace open and directing an air blast directly at the pistons. A cooling curve is shown in figure 7. Even this rapid rate of cooling is not sufficient to prevent recrystallization of some samples. Whenever the presence of water vapor or other volatiles is not necessary to preserve the crystal phase present during the run, the pistons and holders can be removed rapidly and water quenched. The sample in the stainless ring and platinum foil capsule usually separates readily from the piston, and quenching is essentially instantaneous on contact with water. The time to get the sample from test conditions into the water is less than 10 seconds.