

X-RAY OBSERVATION OF CHEMICAL AND POLYMORPHIC EQUILIBRIA UNDER HYDROSTATIC PRESSURES

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Abstract—A pressure vessel has been designed for use with fluid pressures to 5000 bars and temperatures to 300°C in combination with X-ray diffraction examination *in situ*. A narrow X-ray beam is passed through the pressure fluid onto the sample contained within a beryllium cylinder, with pressure being developed by an 'O'-ringed piston.

Examination of various phases within the system $\text{CaSO}_4\text{-H}_2\text{O}$ has revealed the existence of at least one, possibly more new phases, most likely hydrous, that appear to be stable only in the presence of low pressures (to 500 bars). One of these phases can be indexed on the basis of a distorted anhydrite cell with $a = 6.46_9 \text{ \AA}$, $b = 6.81_5 \text{ \AA}$, and $c = 7.14_8 \text{ \AA}$ ($Z = 4$). Gypsum in the presence of a 4 molal NaCl solution has been converted to the hemihydrate phase at $98 \pm 2^\circ\text{C}$ under 100 bars pressure, but no such conversion was observed using distilled water.

Investigation of the conditions of stability of AgI-IV with this vessel and with Van Valkenburg's high-pressure optical device has shown that (1) pure cubic (II') or fine grained mixtures of cubic and hexagonal (II) AgI cannot be completely converted to phase IV within the times allotted, (2) pure hexagonal AgI (II) can be quickly converted to phase IV without polygonization, and (3) the II-III phase boundary is essentially correct as originally determined by Bridgman in 1915.

1. INTRODUCTION

MOST chemical data pertaining to solid-liquid equilibria, as well as certain polymorphic transformations, must be obtained indirectly by means of volume changes, electrical resistivity, or a number of indirect analytical techniques. In most of these instances observation of composition and structure of the resulting solid products is made after the reaction or inversion is complete. Such observations yield results that are usually assumed to pertain to equilibrium conditions, or at least to conditions that existed during formation of the solid product. For example, the formation of AgI from addition of a

potassium iodide solution to a silver nitrate solution appears to result in mixtures of both the hexagonal and cubic type of AgI, or at least it so appears after the filtering, washing and drying processes carried out prior to X-ray examination. X-ray examination during formation *in situ* would not only eliminate this uncertainty but the possible temporary existence of structurally distinct intermediate phases would also be ascertained.

An X-ray device is described below which permits examination of the solid phases involved in chemical or polymorphic processes while reaction and inversion is actually in process. Certain phase relationships in the $\text{CaSO}_4\text{-H}_2\text{O}$ system, and a re-examination of a portion of the AgI phase diagram is presented here as the initial study using this apparatus.

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2. X-RAY FLUID PRESSURE VESSEL

Vessels for the *in situ* study of polymorphic transformations under high pressure and temperature by means of X-rays have been in use several years (Klement and Jayaraman[1], p. 297). However, these vessels function only with nonhydrostatic to partially hydrostatic pressures except for certain vessels operating at high pressures (above 30,000 atm.). Brief mention was made by Adams and Davis[2] of an X-ray vessel using fluid pressures, but no description was given. The present device differs from the one mentioned by Adams and Davis in that the pressure range is slightly lower but the life of the bomb is considerably increased. The present device is considerably less expensive to operate.

Figure 1 is a drawing at half natural size of the present X-ray vessel. The vessel consists of three main parts; a central beryllium cylinder drilled with a 0.180 in. hole to a depth of two-thirds of the cylinder height; a tool-steel (No. 4340, Solar, or No. 883) upper support jacket into which the beryllium cylinder is forced (with about 0.002 in. interference); and a lower jacket that can be screwed onto the upper assembly with sufficient force to apply considerable end-load support. Without such support the beryllium cylinder fails on a surface slightly conical and concentric to the cylinder axis at about 3000 bars whereas with the end-load support pressures up to 4000 bars can be attained. The sample in the form of powder or pellet is placed at the bottom of the blind hole in the beryllium cylinder and several mm of appropriate pressure fluid placed above it. The pressure in the fluid is created by application of thrust from a single or double 'O'-ring piston above it. For polymorphic transformations, dehydration and decarbonation reactions, etc., an inert pressure fluid such as pentane or iso-pentane is used as the pressure fluid. For reactions involving active solutions, these solutions act as the pressure medium as well as part of the X-ray 'window'; or, if no pressure is desired the piston may be

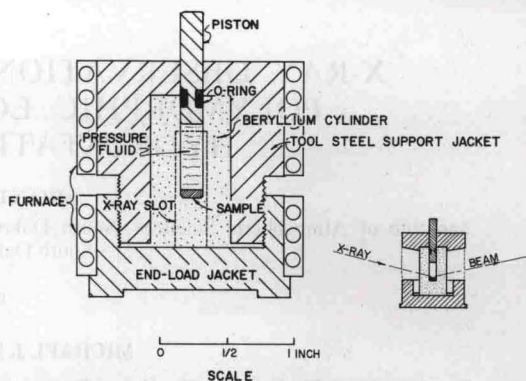


Fig. 1. Schematic diagram of X-ray fluid pressure vessel. Stippled portion is beryllium cylinder. Plane of small diagram (showing slots in support casing and X-ray path) is normal to that of large diagram.

left out of the vessel and the top sealed by a number of methods.

A heating jacket surrounds the exterior of the vessel and is composed of No. 24 Brown and Sharpe nichrome heating element wrapped in fiber glass insulation. A chromel-alumel thermocouple is brought into one of the X-ray windows cut into the upper support jacket and contacts the beryllium cylinder approximately 1/4 in. from the sample. Although the vessel is capable of withstanding 500°C for several hrs (before oxidation of the cylinder requires its replacement) the 'O'-rings cannot maintain more than a few hundred bars pressure above 75°C.

The X-radiation used is restricted to molybdenum ($\lambda = 0.7107 \text{ \AA}$), or one of even shorter wavelength. Considering both the beryllium cylinder thickness (0.625 in.) and bore thickness (0.180 in.), the absorption relation for the X-ray beam passing through the vessel is given by

$$\frac{I}{I_0} = \exp - \left[\left(\frac{\mu}{\rho} \right) \frac{\rho x}{\cos \theta} \right]_c \exp - \left[\left(\frac{\mu}{\rho} \right) \frac{\rho x}{\cos \theta} \right]_f \quad (1)$$

where I is the intensity of the emerging beam, I_0 is the initial beam intensity, (μ/ρ) is the mass absorption coefficient, ρ is the density, and x the diameters of the cylinder c , and pressure fluid f . At $0^\circ 2\theta$ with water pressure