

fluid the absorption of the X-ray beam is 62 per cent, and at  $90^\circ 2\theta$  it is 84 per cent. Within the range of  $5^\circ$  to  $30^\circ 2\theta$  necessary for most studies the resulting diffraction pattern is quite good, especially when scanning at  $1/4$  or  $1/8$  deg  $2\theta/\text{min}$ . The absorption is somewhat less when using pentane as a pressure fluid but the low angle diffraction ring (semi-coherent scatter) of such hydrocarbons makes reading of peaks in the  $5$ – $12^\circ 2\theta$  region more difficult.

Figure 1 also contains a small schematic diagram showing the X-ray slots and the beam path. The only unsupported portion of the vessel is that exposed in the jacket slots. Figure 2 shows the vessel and press mounted in a standard X-ray diffractometer.

Figure 3 presents the calibration data for pressures to 4000 atm., using a single 'O' ring piston. One notes that the up pressure data show very little friction lag. The readings from the calibration curve are considered good to within  $\pm 0.10P$  where  $P$  is the internal pressure within the vessel. The data were obtained using potassium iodide with compression constants of Slater[3].

### 3. INVESTIGATIONS IN THE SYSTEM $\text{CaSO}_4\text{-H}_2\text{O}$

The literature pertaining to phase relations in the system  $\text{CaSO}_4\text{-H}_2\text{O}$  is both vast and confusing. No attempt is made here to review the contributions on the matter but the reader may refer to the summary in Deer *et al.*[4] (p. 202) and to Flörke[5] for fairly complete accounts. The primary interest in the present study was to look for structural changes in gypsum and anhydrite as a result of applied pressure and temperature. The new data presented here does not appear to clear up any of the questions regarding the identities of the hemihydrate, and  $\gamma\text{-CaSO}_4$ .

#### A. Effect of salinity on the gypsum-hemihydrate transformation

The gypsum-anhydrite transformation did not take place using distilled water at temperatures of  $115^\circ\text{C}$  for 12 hrs in the beryllium

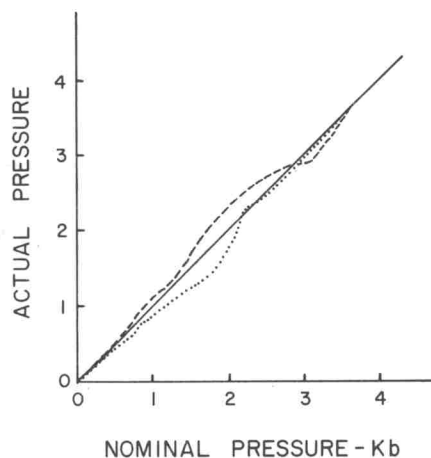


Fig. 3. Pressure calibration of vessel. Compression standard used was KI with pentane pressure fluid.

vessel. The phase described by Posnjak[6] as the hemihydrate was also not observed under these conditions. The piston was placed in the vessel during this experiment but the only pressure developed was that due to the vapor pressure of the super-heated  $\text{H}_2\text{O}$  above the sample. At this temperature this pressure is 25 bars, which would appear insignificant as far as altering the phase relationships is concerned. Thus, for the duration of the experiment, gypsum in pure water persisted metastably beyond the  $42^\circ\text{C}$  inversion for anhydrite and the  $97^\circ\text{C}$  inversion to the hemihydrate.

Similar experiments using gypsum as the starting material were performed using a 4 molal solution of NaCl. The transformation to anhydrite was again not possible for the several hour duration of the run; however, the gypsum was converted at  $98 \pm 1^\circ\text{C}$  and 100 bars pressure to a phase which appears to be the hemihydrate as described by Posnjak[6]. The conversion time was about  $1/2$  hr but an incubation period of about 15 min above the  $97^\circ\text{C}$  transformation point was noted. Figure 4(A) and (B) are direct tracings of the diffractometer record for gypsum and the hemihydrate for the observed transformation *in situ*.

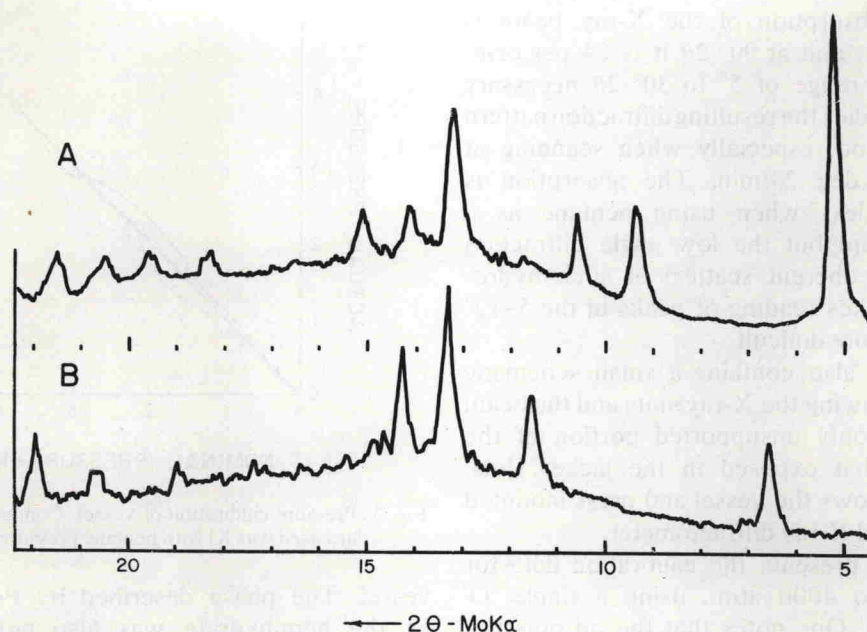


Fig. 4. (A) Diffraction record from X-ray vessel of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in distilled water at  $26^\circ\text{C}$  and atmospheric pressure. (B) Diffraction record from X-ray fluid pressure vessel of  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  (Hemihydrate) formed from gypsum at  $98 \pm 2^\circ\text{C}$  and 100 bars pressure in 4 molal NaCl solution.

The spacing and intensity data are given in Table 1.

#### B. Experiments with anhydrite + water under pressure

A large number of experiments were designed to observe the changes in X-ray pattern of anhydrite in the presence of water, with and without high pressures. Most experiments were carried out at room temperature in the beryllium cylinder under slight pressure, but one experiment was performed by scanning the standard powder 'well' mount with the powder material immersed in water.

In the 'well' mount experiment, as well as those using the cylinder with piston removed, a very pronounced variation with time of certain diffraction peaks of the anhydrite (notably the unresolved  $020+002$  doublet) was observed. In addition to this, certain weaker peaks would appear and disappear within  $1/2$  deg  $2\theta$  of this doublet. Figure 5 is a portion of an oscillation record showing

Table 1. *Interplanar spacings and intensities of  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  formed at  $98 \pm 1^\circ\text{C}$  and 100 bars from gypsum in beryllium vessel\**

$d$ (Å)	$I/I_0$
6.04	32
3.46	33
3.01	100
2.81	47
2.75	10
2.14	10
1.85	30
1.48	5

\* $\text{MoK}\alpha$ , 45 mV, 20 mA,  $1/8$  deg/min. scan speed,  $1/4$  divergence and scatter slits, 0.006 receiving slit.