

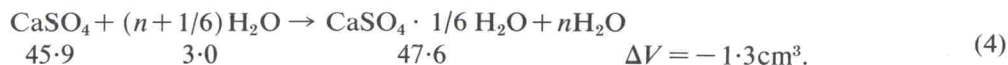
Although the observed changes in X-ray pattern are most likely due to partial hydration, neither the hemihydrate nor gypsum was formed to any degree during any of the experiments. Anhydrite plus water was pressurized at 2000 bars for several hours with no indication of transformation to gypsum. Higher pressure does not enhance the transformation as we have seen above. It seems, therefore, that the phases observed are hydration states of CaSO_4 where n is neither $1/2$, nor 2 , with complete transformation to gypsum being kinetically difficult.

The two peaks with spacings 3.57 and 3.61 Å are unique in that they may be observed in patterns of 'dry' anhydrite and are enhanced and often dominate the pattern at moderate pressures.

Figure 8 shows several tracings of the $11-12$ deg 2θ region of the pattern; (A) is a pattern taken from anhydrite after 3 months open to the atmosphere showing strong development of the 3.61 Å peak. Diagram (B) shows the same material after heating for 3 hrs at 375°C . Figure 8(C) shows almost no $020-002$ doublet of anhydrite but a stronger development of the 3.40 and 3.57 Å peaks observed for the new phase shown in Fig. 7(C). In

ever, the pattern shown in Fig. 7(C) is distinct and enough different from that of anhydrite that closer examination of these spacings is justified. The data of column(B), Table 2 do not fit those of the hemihydrate or $\gamma\text{-CaSO}_4$, but can be indexed easily on the basis of a distorted anhydrite cell with $a = 6.46_9$ Å, $b = 6.81_5$ Å, and $c = 7.14_8$ Å. It appears that if this cell is the correct one the space group may still be B -centered but must be of lower rank than the $Bbmm$ assigned to anhydrite proper. With the cell constants of anhydrite heated to 375°C for 3 hrs (still not completely anhydrous) as $a = 6.19_2$ Å, $b = c = 6.98_8$ Å, we observe 4.5 per cent expansion of the a -axis, 2.5 per cent contraction of the b -axis, and 2.3 per cent expansion of the c -axis, resulting in a cell volume increase of 4.6 per cent.*

Assuming then, that the distorted cell contains four formula units of CaSO_4 , one can determine the theoretical value of n , the hydration coefficient, from a plot of n vs. volume per formula unit (V_c/Z) for the phases anhydrite, hemihydrate, and gypsum (Fig. 9). The resulting value of n for the distorted anhydrite phase is 0.167 . The total molar volume change is thus given by



this pattern a small amount of the 3.61 Å peak may be present. Figure 8(D) shows the anhydrite $020-002$ doublet with the 3.61 Å peak well developed. Control for precise positions for these peaks was obtained by using a quartz internal standard.

That one of more new phases of a possible hydrated CaSO_4 exists under the conditions of these experiments is well demonstrated by the foregoing data. The first set of data in Table 2 contains a mixture of anhydrite peaks and those of the new phase(s) and therefore no attempt at indexing was made. How-

The above relation is not an independent test of the cell but the volume decrement is a result of the position of n on the volume plot of Fig. 9.

It is puzzling that the obvious 3.61 Å peak has not been reported in the literature (Posnjak[6], Jung[7], Weiser *et al*[8], Swanson *et al.*[11], Bunn[12]. Bunn examined material with $n = 0.19$ but did not observe any changes in the X-ray pattern. These

*Axis orientation here is that used by Swanson *et al.*[11].

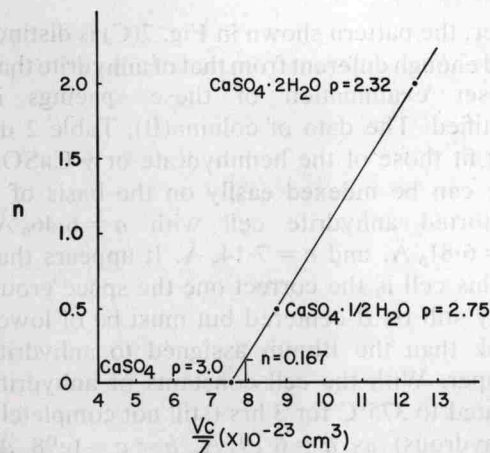


Fig. 9. Plot of hydration coefficient n vs. volume per formula unit (V_c/Z) for gypsum, hemihydrate, and anhydrite. Value of n for distorted anhydrite cell is 0.167.

facts may indicate that slight pressure, less than 100 bars, is required to form the new phase, and, although it is not significant in commercial uses of CaSO_4 its presence might be expected in those stratigraphic sections containing water pressures of this magnitude or higher.

Although there are good reasons for accepting the above cell type for the new phase as correct, the structural relationship to the normal anhydrite cell is not clear. One would expect, for example, that the a -axis (shortest dimension of the anhydrite structure) being that direction parallel to Ca-SO_4 'chains,' would expand less than the b or c axes, whereas b actually contracts. The drastic change in X-ray pattern, does, however, indicate marked structural changes that do not take place easily, but nevertheless are reversible. In view of the lack of the appearance of the hemihydrate in these studies a hydration state equal to $n = 1/2$ was not attained. It is thus concluded here that a definite structural state of hydration with n less than $1/2$ can exist in the $\text{CaSO}_4\text{-H}_2\text{O}$ system.

One notes from Table 2 (*A*) that not all of the spacings have been accounted for by the anhydrite and distorted anhydrite structures. The 3.61 Å peak is especially strong

and seems to develop under pressures greater than that required to form the distorted phase. This and probably other of the new peaks unaccounted for may represent another hydration state, but present data are insufficient to warrant a structural investigation.

4. INVESTIGATION OF THE STABILITY OF AgI-IV

The low-pressure phase IV of AgI (also known as the 3 kbar phase) was discovered by Van Valkenburg[13] and studied further by Adams and Davis[2] and by Bassett and Takahashi[14]. There is no doubt that the phase can be formed but to date no one has established the reality of a true pressure-temperature stability field with respect to the other known polymorphs of AgI. Davis and Adams[15] suggested a positive P - T slope for the II-IV boundary [phase nomenclature is summarized by Bassett and Takahashi[14]] based on a maximum temperature for the II-III-IV triple point of about 50°C and one room temperature point in the diagram for the appearance of phase IV. Because of the slight possibility of the occurrence of phase IV in sub-zero quench products from acetone generators or pyrotechnic devices, it was considered advisable to investigate the stability region of this phase, and in particular, to plot out the II-IV stability boundary.

The same apparatus was used here as for the $\text{CaSO}_4\text{-H}_2\text{O}$ experiments. Some higher temperature data were obtained using the vessel described by Adams and Davis[2] (p. 362) using cornstarch pressure medium. In addition, at the kind invitation of Van Valkenburg, one of us (B.L.D.) observed in his laboratory some pertinent high-pressure optical experiments on single crystals of AgI which will be mentioned below.

A. Results

A large number of runs from 0-30°C with pressure raised in 200 bar increments from 2000-4000 bars were performed on various types of silver iodide. In all cases, transforma-