

# The pressure dependence of the dehydration of gypsum to bassanite

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## Abstract

A new experimental determination of the stability relationships for the dehydration of gypsum to the hemihydrate mineral bassanite at elevated temperature and pressure is described. The experimental method used depends on the observation of very small changes in pressure on the onset of reaction due to the potential volume change in the reaction. The technique yields  $P$ - $T$  data of very high precision for this dehydration reaction, and the method is likely to be of use for other reactions. The experimental  $P$ - $T$  results have been compared with those calculated from existing thermodynamic data for this reaction.

KEYWORDS: gypsum, bassanite, dehydration.

## Introduction

THE present paper deals with the experimental determination of  $P$ - $T$  data for the metastable dehydration reaction involving the conversion of gypsum to the hemihydrate mineral bassanite at pressures up to two kilobars. The results of this work have also been used to re-analyse data in the literature on the mechanical properties of gypsum under the approximate conditions of temperature and confining pressure where this dehydration reaction is known to occur. These results will be published elsewhere.

The present experiments are concerned with the study of the metastable reaction in which gypsum dehydrates to give the hemihydrate mineral bassanite. In the temperature range concerned, the stable phase is anhydrite and hence in order to design an experimental procedure it is necessary to understand the circumstances in which the hemihydrate appears as a metastable alternative.

Posnjak (1938) was the first to point out that the reaction involving the appearance of anhydrite is very sluggish since it requires the nucleation of anhydrite from solution. On the other hand the appearance of the hemihydrate is associated with the dissociation of gypsum at a temperature where the dissociation vapour pressure of the gypsum equals the vapour pressure of a saturated solution. This difference in reaction mechanism is responsible for the prior appearance of the hemi-

hydrate which may later convert to anhydrite through a solution and precipitation mechanism. The fact that the hemihydrate can be produced in fast reactions involving the dissociation of gypsum has led to the recognition of several forms of the hemihydrate as distinguished by their thermodynamic properties (Kelley *et al.*, 1941). Material produced by vacuum dehydration of gypsum has a substantially higher free energy than well-crystallised material, an effect which may be associated with imperfect crystallization. In the present experiments, which were carried out in saturated solutions, the hemihydrate is more likely to develop as well crystallized material.

Special precautions are necessary in experiments which explore the stability conditions associated with metastable phases. In the study of the stability of the hemihydrate in the presence of gypsum in these experiments, it was necessary to avoid the appearance of anhydrite or the rehydration of the hemihydrate formed to give gypsum on quenching. This is known to be a relatively fast reaction even at room temperature. As in the case of the study of the dehydration of brucite—where essentially similar problems arose due to rehydration (see Fyfe, 1958)—a method of direct observation of the progress of reaction has been employed in the present experiments. In this case the pressure generated by the reaction is continuously monitored during the development of very small quantities of the product phase. A special feature of the method is the use of a high-resolution pressure

transducer which permits the detection of the formation of extremely small quantities of the hemihydrate.

This experimental method relies on the fact that the autoclave used is extremely stiff and hence the potential volume change in the reaction at constant pressure is recorded as a pressure change induced in the relatively incompressible fluid phase present (water). Preliminary calculations indicated that the change in molar volume in the reaction was approximately  $5 \text{ cm}^3$  and that therefore it should be possible to detect the progress of the reaction at the 0.05% level with ease. From tables of the molar volume of water at various temperatures and pressures (Burnham *et al.*, 1969) it may be estimated that for water at  $100^\circ\text{C}$  and 1000 bars a volumetric strain of 0.4% is equivalent to a pressure change of approximately 100 bars.

### Experimental method

The apparatus used was that described by Hall *et al.* (1986) and comprised a stainless steel autoclave of  $100 \text{ cm}^3$  interior volume, a needle valve, bursting disc and pressure transducer all having a pressure rating of 2 kbar. The autoclave was wholly submerged in an oil-bath filled with silicone oil. The pressure transducer was of the strain gauge type with a range up to 2 kbar and was calibrated at sixteen equally spaced pressures immediately before the experiment using a dead-weight calibrator. The calibration data from the pressure transducer was fitted to a cubic polynomial which was used in turn during experiments to convert the transducer readings to absolute pressure. The resulting derived pressures were accurate to 0.25 bar. The transducer was mounted well clear of the oil-bath to minimize thermal effects. Temperatures

were sensed by four platinum resistance thermometers strapped around the body of the autoclave. The temperature readings were averaged and the temperature thus derived was estimated to be correct to  $\pm 0.25^\circ\text{C}$ .

The pressure and temperature transducers were monitored during the experiments by a Solartron Orion Delta data logger which also controlled the bath temperature programme using a fifth platinum resistance thermometer in the circulating oil. The combination of high quality input signal handling, process control outputs and high level language made the logger an ideal experiment control computer. The experimental set-up is illustrated schematically in Fig. 1 and in the photograph provided in Fig. 2.

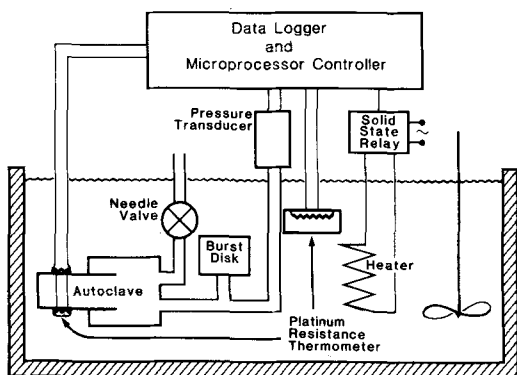


FIG. 1. A schematic diagram showing the essential features of the apparatus.

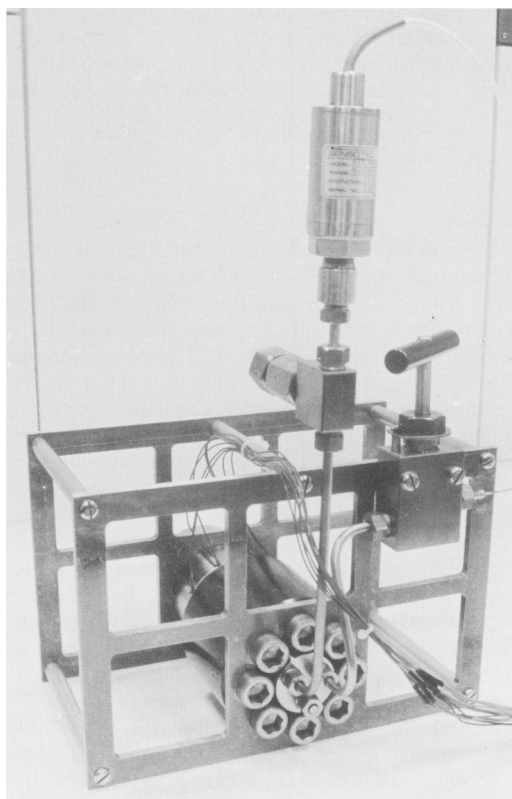


FIG. 2. The assembled autoclave prior to immersion in the oil-bath.

For the present series of experiments AR calcium sulphate dihydrate was firmly packed into the autoclave and saturated with distilled water. A pad of glass microfibre was placed on top of the powder

to retain it in position and, on closing the autoclave, all remaining void space was filled with distilled water. The sealed autoclave was placed in the oil-bath and heated to temperature during which process a substantial pressure was generated due to the potential thermal expansion of the water present. The needle valve was used to lower this pressure at intervals and finally to set the pressure close to that for the dehydration reaction at a temperature also just below that of the dehydration  $P$ - $T$  curve. At this point the bath heating programme was placed under the control of the logger which introduced step heating in  $0.25\text{ }^{\circ}\text{C}$  increments, dwelling for two and a half hours at each temperature and logging both pressure and temperature at regular intervals.

It was found that, while the system remained within the stability field of gypsum, the internal pressure stabilized within half an hour but, when the system passed into the stability field of the hemihydrate, the internal pressure did not stabilize but rose monotonically at a rate which increased regularly with each temperature increment. Determination of the threshold temperatures at which

pressure stabilization failed to occur could be made more precisely from plots of  $dP/dt$  versus  $t$ , where  $t$  represents the time from the commencement of data logging. From the assembled data it was possible to define the onset of the dehydration reaction at a number of different pressures. An example of one such set of data is shown in Fig. 3 and the final  $P$ - $T$  curve for the gypsum to bassanite transformation in Fig. 4. The  $P$ - $T$  curve utilizes the single point at one atmosphere obtained by Posnjak (1938), which gave a temperature of  $97.5\text{ }^{\circ}\text{C}$  for the dissociation of gypsum, and the appearance of the hemihydrate, in a saturated solution.

### Thermodynamic parameters

Kelley *et al.* (1941), in a thermodynamic study of the dehydration products of gypsum, indicated that there were several different structural modifications of the hemihydrate phase for which thermodynamic parameters were determined. The beta form of the hemihydrate may be prepared from gypsum by vacuum dehydration at  $100\text{ }^{\circ}\text{C}$ , i.e. in the absence of solution (McConnell, 1965). The

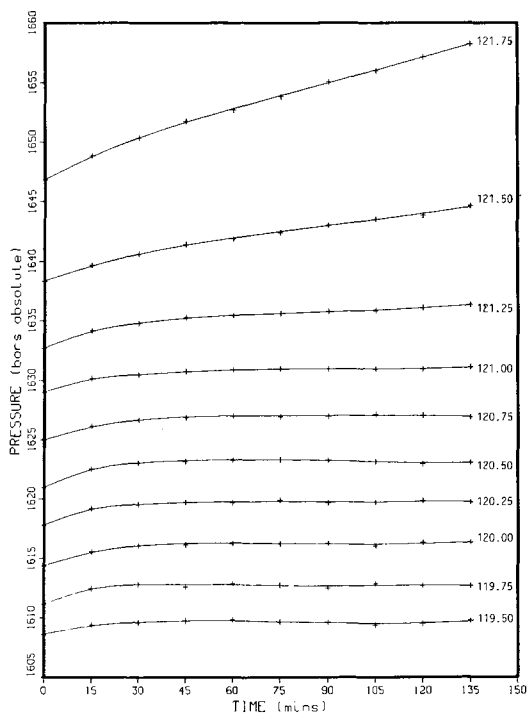


FIG. 3. Recorded pressure measurements at a series of increasing temperatures in the immediate vicinity of the  $P$ - $T$  univariant conditions for gypsum-hemihydrate co-existence.

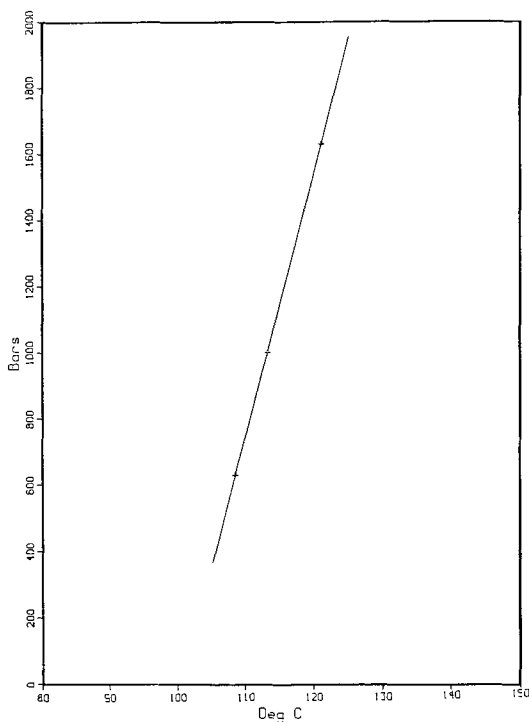


FIG. 4. The final experimentally determined univariant  $P$ - $T$  plot for the co-existence of gypsum and the hemihydrate.

alpha form is normally prepared from saturated solutions and is a well crystallised phase. In the present analysis it will be assumed that the hemihydrate phase formed in the autoclave is the alpha form.

Data on the coexistence of gypsum and the hemihydrate in solution at one bar were obtained by Posnjak (1938). The coexistence temperature was determined as 97.5 °C from solubility measurements on both phases. The slope of the univariant  $P$ - $T$  line for the coexistence of the hemihydrate and gypsum can be calculated from thermodynamic data presented in Kelley and King (1961) on the entropy and specific heat data for these phases.

Table 1. Entropy and specific heat data for gypsum and the hemihydrate at 298.15 K

	$S$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$C_p$ (cal mol <sup>-1</sup> K <sup>-1</sup> )
Gypsum	46.4±0.3	44.5
Hemihydrate	31.2±0.4	28.6

At the observed coexistence point of gypsum and the hemihydrate at 112.5 °C and one kilobar the entropy change associated with the reaction to produce the hemihydrate and water was calculated as 12.22 cal mole<sup>-1</sup> K<sup>-1</sup>. In this calculation the entropy difference at 385.65 K was adjusted with respect to  $\Delta C_p$ . The entropy contribution of the water formed as liquid was evaluated from the entropy data available in Burnham *et al.* (1969). The volume change for the reaction was determined using the data on the specific volume of water given in Burnham *et al.*, 1969, and densities for gypsum and the hemihydrate of 2.32 and 2.74 g cm<sup>-3</sup> respectively. The change in molar volume was found to be 5.99 cm<sup>3</sup>.

Using these calculated values for the entropy and volume change in the dehydration reaction the slope of the  $P$ - $T$  line for the coexistence of gypsum and the hemihydrate at 385.65 K and 1000 bars was calculated to be 85.5 bars K<sup>-1</sup>, which is close to the experimentally measured value of 81.1 bars K<sup>-1</sup>. Errors in the calculated slope of the  $P$ - $T$  curve at 385.65 K and 1000 bars are unlikely to exceed ±5 bars K<sup>-1</sup> as determined by the uncertainty in the entropy values given by Kelley and King (1961) and quoted in Table 1. It is probably worth commenting on the fact that the  $P$ - $T$  plot of Fig. 4 does not easily pass through the data point at one bar and

97.5 °C even when attention is paid to the reduction in slope of the  $P$ - $T$  curve at low pressures. Calculation indicates a value of slightly below 100 °C for the extrapolation. This may be due to a systematic error in the determination of the internal temperature of the autoclave (which is considered unlikely), or it may be due to the fact that the mechanism of the dehydration reaction involves the dissociation of gypsum in the first instance and hence may impose some degree of imperfection on the hemihydrate product. This is consistent with the fact that thermodynamic data due to Kelley *et al.* (1941) indicate that the theoretical temperature of coexistence of gypsum with the beta form of hemihydrate at one bar pressure can be calculated as 400 K (136.9 °C). One further effect may be cited. This relates to the fact originally demonstrated by Fyfe (1958) that the hydration and dehydration of magnesium hydroxide shows a degree of hysteresis since the final equilibrium state as approached from both directions differs somewhat. A similar observation was made by McConnell (1965) in isothermal hydration-dehydration studies on soluble anhydrite. In this case a zone of very low rates of hydration and dehydration existed close to the equilibrium vapour pressure at fixed temperature. Such low rates must produce a hysteresis effect in short term experiments and hence limit the accuracy with which the equilibrium state can be defined, even for a relatively fast reaction.

In the experiments described here there was ample opportunity to observe the reverse reaction involving the reappearance of gypsum but this reaction was not observed in long-term experiments. In such experiments the reappearance of gypsum should be accompanied by a fall in pressure under isothermal conditions.

## Conclusions

The present observations on the development of the hemihydrate mineral bassanite at the expense of gypsum under conditions of high water pressure are entirely consistent with existing thermodynamic data on this dehydration reaction and are likely to be representative of the metastable coexistence of these two phases in the absence of the stable phase anhydrite. The experiments also suggest that this metastable reaction is likely to be dominant in mechanical experiments on gypsum at temperatures where dehydration occurs (Heard and Rubey, 1966; Murrell and Ismail, 1976, and Fig. 3 of Murrell, 1985) and this behaviour can be modelled precisely by using the data available here. Two situations exist in the context of such mechanical texts as already described by Murrell (1985). In the first of these the pressure of the fluid is equal to the

confining pressure in a mechanical test. In the second. fluid pressures within pores in the sample may be substantially less than the total confining pressure, at least prior to the failure of the sample, and the reduced free energy of the fluid phase results in a lowering of the equilibrium temperature for the reaction at a given confining pressure. The equilibrium pore pressure is buffered by the extent of reaction, and can be calculated from the new data as a function of confining pressure and temperature as described by MacDonald (1953). The calculated equilibrium pore pressures may then be used to establish the effective confining stress in gypsum samples in mechanical tests under isothermal conditions.

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