Infrared Spectroscopic Studies of Calcium Sulphate heated to High Temperatures

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Infrared spectroscopic investigations have shown that on the basis of changes in the ν_3, SO_4 band which occur when calcium sulphate is heated from 400° to 1400 °C, there are two forms of insoluble anhydrite, designated as β'- and β-$CaSO_4$. β'-$CaSO_4$ is metastable and is completely converted into β-$CaSO_4$ by heating above 1000 °C. With longer heating periods this conversion can even take place at lower temperatures. β-$CaSO_4$ is stable and is of the same type as the naturally occurring form of anhydrite.

Several forms of calcium sulphate have been recognised within the system $CaSO_4 - H_2O$ [1, 2], viz. gypsum ($CaSO_4 \cdot 2\,H_2O$), hemihydrate ($CaSO_4 \cdot \frac{1}{2}\,H_2O$), soluble anhydrite ($\gamma$-$CaSO_4$), insoluble anhydrite ($\beta$-$CaSO_4$) and high temperature anhydrite (α-$CaSO_4$). Hemihydrate and soluble anhydrite have both been reported to exist in two forms, the so-called α- and β-varieties [1]. (These α- and β-forms should not be confused with β-$CaSO_4$ and α-$CaSO_4$, which refer to insoluble and high temperature anhydrite respectively.) The existence of α-$CaSO_4$ above 1200° has been mentioned [2–5], but some workers have cast doubt upon its existence [6, 7].

In previous work on the dehydration of $CaSO_4 \cdot 2\,H_2O$ different infrared absorption spectra were obtained for gypsum, hemihydrate, soluble anhydrite and insoluble anhydrite; no noteworthy spectral differences were obtained between the so called α- and β-forms of hemihydrate or soluble anhydrite [8]. This showed that there are no significant structural differences between the respectively α- and β-forms. Small differences in properties as may arise can be attributed to differences in the surface areas [9, 10].

The infrared spectra of γ-$CaSO_4$ and $CaSO_4 \cdot \frac{1}{2}\,H_2O$ have shown strong similarities in their SO_4 bands [8].

γ-$CaSO_4$ is essentially a dehydrated hemihydrate, since it is basically a hemihydrate lattice from which the H_2O molecules have been removed. The hemihydrate structure is open and includes channels through which water molecules can migrate; certain sites are more energetically favourable for their retention; when these sites are all occupied, the formula of hemihydrate $CaSO_4 \cdot \frac{1}{2}\,H_2O$ is achieved [11]. It is the removal of this water from the channels in the hemihydrate lattice that gives rise to the γ-$CaSO_4$ structure. γ-$CaSO_4$ is usually associated with up to 0.9% H_2O in practice [12], and readily rehydrates back to the hemihydrate.

As a continuation of these studies, the infrared spectra of $CaSO_4$ have been investigated further, after heating the samples from 400 °C to 1400 °C.

Experimental

Various samples of A.R. $CaSO_4 \cdot 2\,H_2O$ (obtained from British Drug Houses Limited, Poole, Dorset) were heated at constant temperature within the range 400 –

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1400 °C in a muffle furnace for intervals of time between 1 and 6 hours. Immediately after cooling the samples in a desiccator, the infrared spectra were recorded on a Unicam SP200 G spectrophotometer in the region $650-4000\,cm^{-1}$, using both KBr discs and Nujol mulls. These specimens were also examined by X-ray diffraction on a Philips' diffractometer using the CuK_α line. Some of the samples were checked by DTA and refractive index measurements.

Results and Discussions

In Fig. 1, the infrared spectra of $CaSO_4$ samples heated from 400 °C to 1400 °C at intervals of 100 °C and recorded as Nujol mulls have been reproduced in the region $1000-1250\,cm^{-1}$. It can be seen that the ν_3, SO_4 vibration shows different behaviour in the spectra of the samples heated from 400° to 1300 °C. Two types of band structure are evident. In one case splitting is shown with maxima at 1095 and 1158 cm^{-1}. The characteristic contour of this band remains dominant in the spectra of the samples heated from 400° up to 600 °C (Figs. 1A, 1B and 1C). For the samples heated to 700°, 800°, 900° and 1000 °C, the details within the band are lost (curves D, E, F and G in Fig. 1). With the samples heated to 1100 °C, however, a different pattern with the ν_3, SO_4 band appears. The shape of this band becomes quite distinct and remains the same in the specimen heated to 1200 and 1300 °C. The values of the two frequencies are 1130 cm^{-1} and 1158 cm^{-1}. A lack of band structure in the sample heated to 1400° is indicative of decomposition of the calcium sulphate having been fully effected: $CaSO_4 \rightarrow CaO + SO_3$. A slight decomposition was also possible in the samples heated to 1300 °C and to a much lesser degree in those at 1200 °C.

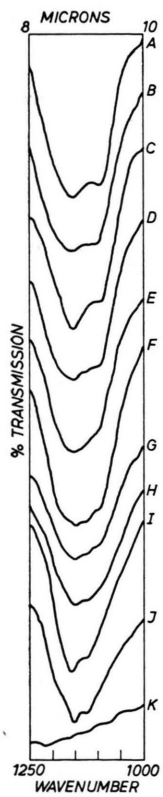

Fig. 1. Infrared Spectra of $CaSO_4$ heated to A—400 °C, B—500 °C, C—600 °C, D—700 °C, E—800 °C, F—900 °C, G—1000 °C, H—1100 °C, I—1200 °C, J—1300 °C, K—1400 °C, as Nujol mulls in the region $1000-1250\,cm^{-1}$.

The above spectral features can be explained on the basis of slight modifications occurring in the molecular structure of $SO_4^{2\ominus}$ ions within the calcium sulphate lattice with temperature rise from 400° to 1300 °C. One type of modification remains dominant between 400° and 600 °C (referred to as β'-$CaSO_4$), whilst the other starts forming at 700° and the formation is complete above 1000 °C, (β-$CaSO_4$) depending upon the time of heating; the longer this is, the lower the temperature at which the spectral features of the high temperature form become clear. There are no specific temperatures corresponding to a rapid interconversion of the two forms. Around 700° – 1000 °C, mixtures of these two forms can arise.

Such detection of two modifications of insoluble anhydrite by infrared spectroscopy seems to confirm the postulation by GAUBERT [13] and DUBUISSON [14] of two forms of this anhydrite. The modification β'-$CaSO_4$ appears to be metastable, since it slowly converts to the β-form with time. Also, the conversion has been observed under pressure whilst preparing the KBr discs for infrared measurements. This latter modification (β-$CaSO_4$) is stable and the same variety exists as the naturally occurring anhydrite, which is a well known mineral [15].

The infrared spectral data of β- and β'-$CaSO_4$ are given in Table I along with those of γ-$CaSO_4$, hemihydrate and gypsum for comparison purposes.

X-ray diffraction studies showed that there is a net increase in the sharpness of the d-lines with the samples heated from 400° to 1300 °C, although

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Insoluble Anhydrite (High Temperature Form)	Insoluble Anhydrite (Low Temperature Form)	Soluble Anhydrite	Hemihydrate	Gypsum	Tentative Assignments
675 s	673 s	665 s	660 s	667 s	ν_4, SO_4
	1012 vw	1008 vw, 1012 vw	1008 m	1004 vw	ν_1, SO_4
	1095 s	1092 s	1094 s		
		1115 s	1115 s	1120 vs	
1130 s		1135 sh	1135 sh	1145 vs	ν_3, SO_4
1158 vs	1158 vs	1155 vs	1155 vs	1155 sh	
		1168 sh	1168 sh		
			1623 s	1623 s, 1688 m	ν_2, H_2O
			2030 vw		$2 \times \nu_1$, SO_4
			2090 vw		
2130 vw	2130 vw	2150 vw	2130 vw	2130 w	$\nu_1 + \nu_3$, SO_4
2230 vw	2230 vw	2230 vw	2220 vw	2230 vw	$2 \times \nu_3$, SO_4
				3245 vw	$2 \times \nu_2$, H_2O, $\nu_3 H_2O$
				3410 s	ν_1, H_2O
			3560 m	3500 w	ν_1, H_2O
			3615 s	3555 m	ν_3, H_2O

Table I. Infrared spectral data for the various forms of calcium sulphate. vw = very weak, w = weak, m = medium, vs = very strong, s = strong, sh = shoulder.

the values of the d-spacings were found to be similar in all cases. This was interpreted as indicating that the differences betwes the two types of insoluble anhydrite, β'- and β-$CaSO_4$, are a second order effect i. e., the basic orthorhombic lattice is present in both forms and the differences appear to be due to different stacking arrangements within the crystal lattice. Such changes could account for the differences observed in the infrared spectral data. The conversion might be instigated by slight decomposition ($\sim 1\%$ or less) of some anhydrite into calcium oxide. With the conversion of $\beta' \rightarrow \beta$-$CaSO_4$ the specimen becomes progressively more crystalline with rise in temperature.

Optical microscopic measurements also supported the above view. A typical sample heated in the range 400° to 600 °C consisted of long laths and had moderate birefringence and shadowy extinction, the refractive index lying between 1.54 and 1.56. The sample looked like a dehydrated gypsum. Another specimen heated to 1200 °C was shown to consist of irregular globular birefringent crystals. The refractive index in this case lay between 1.57 and 1.61, similar to natural anhydrite [15]. These crystals resembled those of natural anhydrite.

DTA studies were performed on a Stanton's Standata 6 – 25 differential thermoanalyser, and revealed a continuously increasing slope of the base line up to 1200 °C after the formation of the exotherm at 350 °C due to the conversion of soluble anhydrite (γ-$CaSO_4$) into insoluble anhydrite. A sharp endotherm was obtained at 1222 °C, owing to the formation of high temperature anhydrite (α-$CaSO_4$). A broad endotherm above 1400 °C represented the melting point of $CaSO_4$. Upon cooling, exotherms

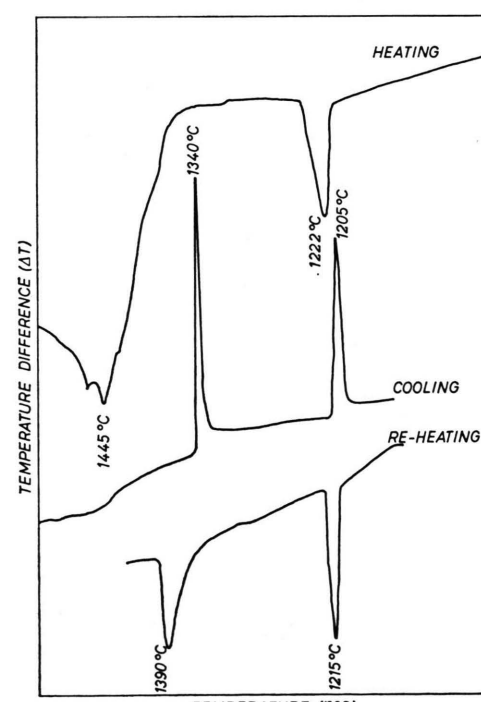

Fig. 2. DTA curves of calcium sulphate at high temperature obtained upon heating, cooling and re-heating, respectively.

were obtained at about 1340 °C and 1205 °C, corresponding to the formation, with some hysteresis, of α-$CaSO_4$ from its constituent oxides and the inversion of α- to β-$CaSO_4$, respectively. Upon reheating the sample, endotherms at 1215 °C and 1390 °C were obtained, corresponding, respectively, to the β- to α-$CaSO_4$ inversion and the decomposition of α-$CaSO_4$:

$$CaSO_4 \rightleftarrows CaO + SO_3 .$$

The above DTA curves are shown in Fig. 2.

In order to ascertain that the endotherm just above 1200 °C was due to α-$CaSO_4$ and not to the formation of a high temperature modification of insoluble anhydrite stable at room temperature, some anhydrite, which had been heated to 1300 °C and quenched was examined by DTA. A similar endotherm was again obtained, suggesting that α-$CaSO_4$ is stable only at high temperatures greater than about 1215 °C and converts to β-$CaSO_4$ upon cooling. These studies thus confirm that α-$CaSO_4$ (high temperature anhydrite) could not be stabilized below 1200 °C by quenching and that this modification should not be confused with β- and β'-$CaSO_4$.

The following scheme summarizes the reactions that take place upon heating γ-$CaSO_4$ (soluble anhydrite) from 400° to 1300 °C.

γ- ↓ $CaSO_4$ 400° – 600 °C

β'- ↓ $CaSO_4$ (metastable state) 700° – 1200 °C

β- ↓ $CaSO_4$ (natural anhydrite) 1215 °C

α- ↓ $CaSO_4$ * 1400 °C

$CaO + SO_3$

↓ on cooling

α- ↓ $CaSO_4$ *

↓ 1205 °C

β- ↓ $CaSO_4$

Conclusion

Infrared spectral studies of calcium sulphate after heating from 400° to 1400 °C show that there appear to be two types of insoluble anhydrite. The low temperature variety (β'-$CaSO_4$) formed between 400° and 600 °C is a metastable form which converts into the high temperature variety (β-$CaSO_4$) either by heating between 700° and 1300 °C depending on the time of heating, or upon standing for several months. β-$CaSO_4$ is more crystalline and is stable, it is the same type as natural anhydrite. The two forms β'- and β-$CaSO_4$ differ considerably from monoclinic α-$CaSO_4$, which is stable only above 1200 °C.

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* Only stable at high temperatures.