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Note

Detection and quantitative determination of $CaSO_4 \cdot 2H_2O$ in $CaSO_4 \cdot \frac{1}{2}H_2O$ using calorimetric DTA

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General

The setting of plaster is strongly influenced by small amounts of dihydrate (Fig. 1). Reliable analytical methods for determining small quantities of $CaSO_4 \cdot 2H_2O$ ($\leqslant 1\%$) in $CaSO_4 \cdot \frac{1}{2}H_2O$ (hemi-hydrate) are therefore of considerable interest.

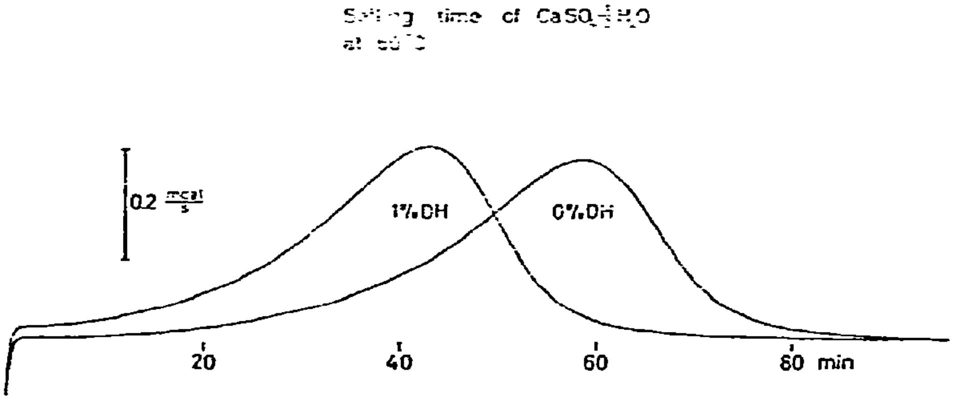

Fig. 1. Setting time of $CaSO_4 \cdot \frac{1}{2}H_2O$ at 50°C (isothermal) as a function of dihydrate content.

Until now, indirect gravimetric methods are used, which are based on partial and complete hydration to determine soluble anhydrite and hemi-hydrate content and which use complete dehydration at 350°C to determine the total content of dihydrate (DH) and hemi-hydrate (HH). Thus, the result of the dihydrate determination is dependent on three different—however time-consuming—procedures, whose errors may cumulate in the worst case. The typical (not the maximum) error is estimated to be ±50%, i.e. a dihydrate content of 1.0% could be determined to ±0.5% absolute.

This explains the interest for a direct, reliable and more accurate method. Since $CaSO_4 \cdot 2H_2O$ shows a typical endothermic dehydration reaction to $CaSO_4 \cdot \frac{1}{2}H_2O$ (Fig. 2), an approach was made, using calorimetric methods, i.e. quantitative DTA.

Problem description

Small quantities ($\leqslant 1\%$) of dihydrate (DH) are to be detected in a large excess of hemi-hydrate by means of high sensitivity quantitative DTA.

High accuracy and precision as well as a detection limit below 0.1% dihydrate should be achieved.

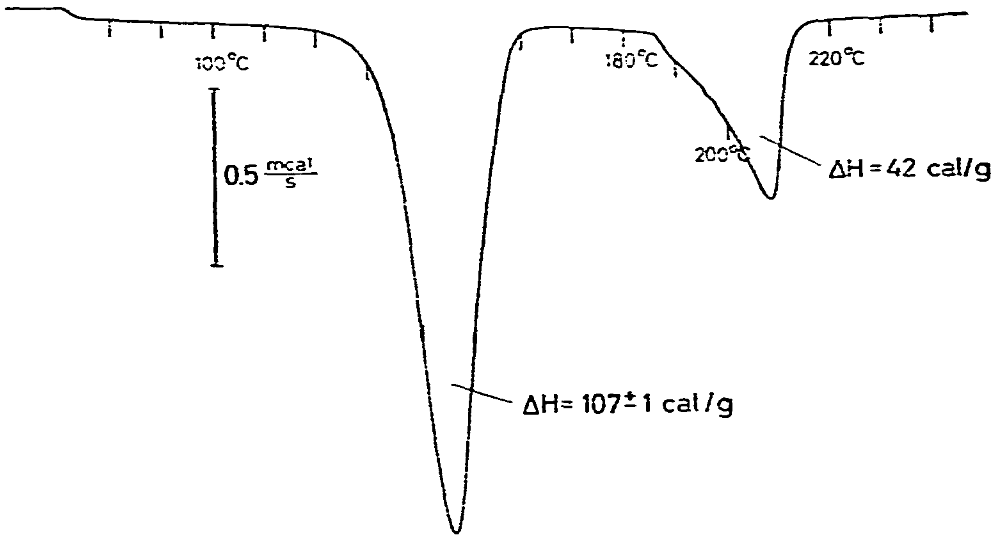

Fig. 2. Resolution of dehydration peaks and determination of dehydration enthalpies of pure $CaSO_4 \cdot 2H_2O$ (Merck 2161).

Requirements

(1) An analytically valid determination of the dihydrate is only possible if one succeeds to separate the DTA peaks due to physically adsorbed water and the two well-known dehydration reactions

$$CaSO_4 \cdot 2H_2O \rightleftharpoons CaSO_4 \cdot \tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O(g)$$

and

$$CaSO_4 \cdot \tfrac{1}{2}H_2O \rightleftharpoons CaSO_4 + \tfrac{1}{2}H_2O(g)$$

as completely as possible.

(2) The demand for high sensitivity (low detection limit) requires an open system in order to take advantage of the high heat of vaporization of water (540 cal g^{-1} at 100°C).

(3) The reaction enthalpy of the first dehydration reaction, i.e., the total of decomposition and vaporization enthalpies, must be known as accurately as possible since it is the basis of the absolute analytical detection of the dihydrate content.

EXPERIMENTAL

All experiments were performed on a commercial Mettler TA2000 unit[1].

The requirements mentioned above, however, require a special experimental technique since, on the one hand, a good separation of peaks can only be achieved in an atmosphere of sufficiently high water vapour pressure and, on the other hand, free evaporation of water vapour must be guaranteed in order to achieve high detectability.

To solve this problem, the normal sealing technique for our aluminium crucibles was modified: instead of producing gas-tight seals by cold welding crucibles and lids, inert α-alumina was imbedded in the rim, thus generating capillary leaks with the desired properties: possibility for free evaporation of water and nevertheless generation of an atmosphere of sufficiently high water vapour pressure by the sample.

Applying this sealing technique, resolution of DTA peaks due to physically adsorbed water and the two dehydration reactions was achieved in a "quasi open system" and quantitative evaluation of related enthalpies (peak areas) was possible (Figs. 2 and 3).

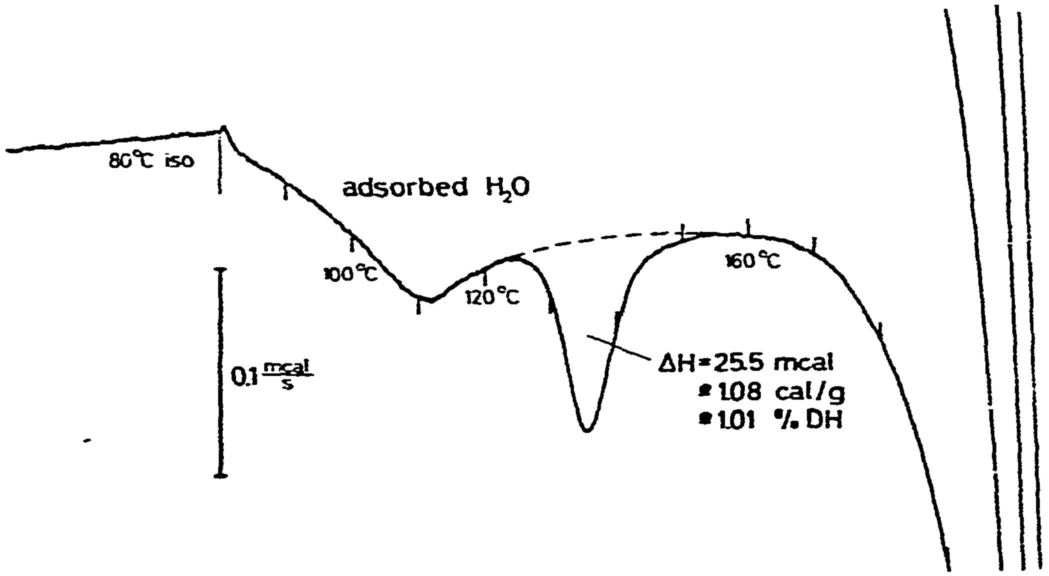

Fig. 3. Detection and determination of dihydrate between desorption of physically adsorbed water and dehydration of hemi-hydrate.

Reaction enthalpies of the two dehydration reactions were measured using an on-line configuration with a Mettler data transfer system and a Hewlett-Packard HP9810A calculator for direct and rapid peak evaluation[2]. 2–8 mg samples of analytical grade $CaSO_4 \cdot 2H_2O$ (Merck 2161) were examined.

The test samples of known dihydrate content (0%; 0.5%; 1.0%) were analyzed for the reaction enthalpy related to the first dehydration reaction with an amplifier range of 0.3 mcal sec^{-1} f.s.d. and typical sample sizes of 20 mg. Samples were preconditioned to constant signal at 80°C (in order to evaporate a part of the physically adsorbed water) and then scanned at 1 °C min^{-1} or 2°C min^{-1}. Nitrogen at 20 ml min^{-1} was used as a purging gas (Fig. 3).

RESULTS AND DISCUSSION

1. *Reaction enthalpies*

The reaction enthalpy according to the equation

$$CaSO_4 \cdot 2H_2O \rightleftharpoons CaSO_4 \cdot \tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O(g)$$

was found to be 107±1 cal g^{-1} dihydrate or 18.42 kcal mol^{-1} at 130°C, which is in excellent agreement with 108 cal g^{-1} or 18.62 kcal mol^{-1} reported in the literature[3]. The analytically relevant constant K is obtained by inverting the specific reaction enthalpy:

$$K = \frac{1}{107} \quad [\mathrm{mg\ mcal^{-1}}]$$

$$= 0.0093_5\ [\mathrm{mg\ mcal^{-1}}]$$

which means, that an observed enthalpy change of 1 mcal corresponds to the presence of 9.3_5 μg of dihydrate. Since in this case 1 mcal also represents the calorimetric detection limit of the instrument, the detection limit for the dihydrate analysis is easily calculated to be 0.05%, assuming a typical sample weight of 20 mg.

The dehydration enthalpy of the hemi-hydrate to anhydrite was found to be 42 cal g^{-1} at 200°C, a result slightly lower than the 46.5 cal g^{-1} calculated from literature data[3].

2. *Test samples*

The results were calculated from the peak area ΔH [mcal] corresponding to the first dehydration reaction (Fig. 3), the constant $K = 0.0093_5$ [mg $mcal^{-1}$] and the sample weight E [mg], according to the following formula:

$$\%\mathrm{DH} = \frac{\Delta H \cdot K}{E} \cdot 100\%$$

They are listed in Table 1.

Mean values and estimated standard deviations give evidence that the described calorimetric method can be successfully applied for direct and comparatively rapid dihydrate determination.

Accuracy and precision are within ±0.05% absolute or better and the detection limit is as low as 0.05% dihydrate.

TABLE 1

RESULTS OF DIHYDRATE ANALYSIS WITH TEST SAMPLES OF KNOWN DIHYDRATE CONTENT

Test sample	*Sample weight, E (mg)*	*Dehydration enthalpy, ΔH (mcal)*	*Specific enthalpy (mcal mg^{-1})*	*Dihydrate content (%)*	
1 0% DH	22.95	0	0	0	
	22.41	12.8	0.57	0.53	
2	22.18	12.1	0.54	0.51	
0.5% DH	31.44	19.8	0.63	0.59	0.53 ± 0.05
	21.30	11.1	0.52	0.49	
	23.21	13.7	0.59	0.55	
	22.20	23.9	1.08	1.01	
	22.62	24.0	1.06	0.99	
3	22.60	25.9	1.15	1.07	
1.0% DH	23.42	24.0	1.02	0.96	1.01 ± 0.05
	23.81	25.3	1.06	0.99	
	23.30	26.3	1.13	1.05	

ACKNOWLEDGEMENTS

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3 *Ullmanns Encyklopädie der technischen Chemie*, Vol. 8, 1957, p. 106.