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Note

The dehydration of disodiumpentacalcium sulphate trihydrate, $Na_2Ca_5(SO_4)_6 \cdot 3H_2O$

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Bock[1] has studied the solubility of gypsum ($CaSO_4 \cdot 2H_2O$) in sodium chloride solutions at temperatures up to 323K. When this temperature range was extended to 383K by Marshall and Slusher[2], evidence was found for the formation of a double salt. This was identified as $Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$ which had been discovered earlier by Hill and Wills[3].

Powell[4] and Glew and Hames[5] prepared the compound and showed by X-ray diffraction that it was isomorphous with calcium sulphate hemihydrate, and suggested that substitution of one calcium ion by two sodium ions had occurred:

$$6CaSO_4 \cdot 2H_2O + 2Na^+ = Na_2Ca_5(SO_4)_6\ 3H_2O + Ca^{2+} + 9H_2O$$

The same authors carried out DTA runs on the compound (hereafter called P.S.[5]) and showed that it decomposed at higher temperatures than $CaSO_4 \cdot \frac{1}{2}H_2O$, and the present work is intended to compare the dehydration of P.S. with the normal hemihydrate[6, 7].

EXPERIMENTAL

Material

Analar grade NaCl and $CaSO_4 \cdot 2H_2O$ were used for the preparation of P.S. The preparation proved difficult and attempts to repeat the published methods, using 6.4M NaCl solutions at 338K, failed. P.S. was finally prepared by using sodium chloride solutions saturated at room temperature, which were heated at 343K for 6 days with 0.14 mol l^{-1} of $CaSO_4 \cdot 2H_2O$. The product was filtered hot and washed with saturated NaCl solution, then acetone and finally dried in a vacuum desiccator. X-ray diffraction confirmed the work of Powell[4] in that the product gave a virtually identical pattern to that of $CaSO_4 \cdot \frac{1}{2}H_2O$. No peaks due to NaCl or any of the other forms of $CaSO_4$ were detected and chemical analysis showed that the material contained 5.01% Na (Theory = 5.25%). Dehydration at 700K gave a weight loss of 6.20% (Theory = 6.15%). Differential thermal analysis (heating rate 20°C min^{-1})

gave a single endotherm with the peak maximum at 543K. This is in agreement with the temperatures previously determined[4, 5].

Kinetic studies

The kinetics of dehydration at atmospheric pressure were followed by measuring the weight loss from powdered samples (100 mg ± 10 mg) on a C.I. Microforce balance (sensitivity 10 mg, f.s.d.) coupled to a potentiometric recorder. Isothermal runs were carried out using boiling solvents[6, 7] and variable temperature runs used an electric furnace and temperature programmer (Stanton Redcroft). Heating rates were low (0.5–2.0° $\min^{-1}$). Various partial pressures of water vapour were obtained by passing nitrogen (70 ml $\min^{-1}$) through drying agents, thermostatted water or salt solutions and then over the sample.

RESULTS AND DISCUSSION

The compound decomposed in a single stage with the weight loss given above, corresponding to loss of three water molecules per mole of P.S.

For the isothermal runs, the proportion decomposed, α, was plotted as a function of time. All of the curves were deceleratory in shape, and reduced time plots[8] showed that the best fit between experimental and theoretical curves was in terms of a one-dimensional diffusion process, following the parabolic law $\alpha^2 = kt$. Isothermal runs were carried out at each partial pressure of water vapour used and at several temperatures between 450 and 490K. No change in the reaction mechanism could be detected. Figure 1 shows some typical experimental data superimposed on theoretical curves.

TG runs were then carried out at the same partial pressures of water vapour,

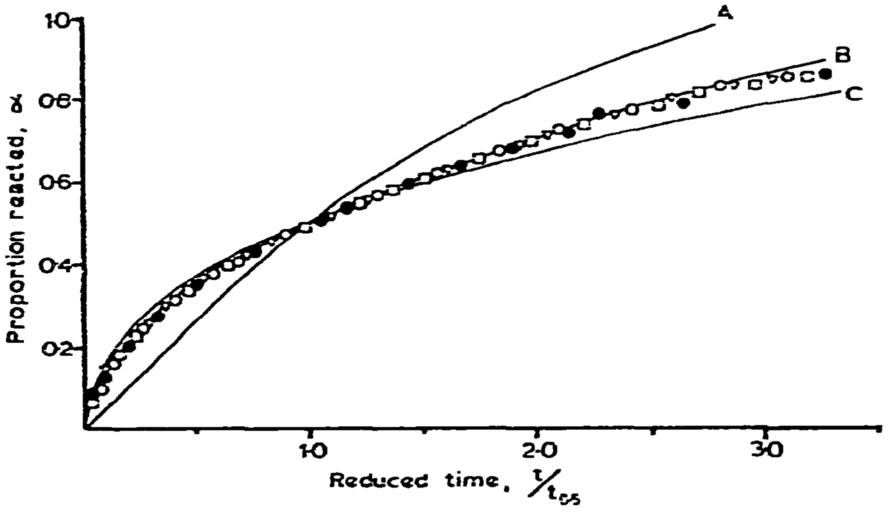

Fig. 1. Comparison of experimental and theoretical reduced time curves. Curve A = "Contracting disc" equation; Curve B = parabolic law; Curve C = 2-dimensional diffusion. ●, 453K/1.06 kNm^{-2}; ○, 464K/2.6 kNm^{-2}; ■, 484K/0.013 Nm^{-2}; □, 490K/1.06 kNm^{-2}.

up to 750K, and activation energies and frequency factors were calculated from the experimental data by the methods of Satava and Skvara[9]. This method involves graphical comparison of the experimental curves with a derived curve which is a function of mechanism and Arrhenius parameters. The method can readily be used even when neither of these variables is known, but previous knowledge of the mechanism makes the determination of the activation energy much more accurate. The range of theoretical models considered was the same for both isothermal and TG runs.

The results of these calculations are shown in Table 1.

TABLE 1

Partial pressure of water vapour	*Activation energy (mol^{-1})*	*Frequency factor A (sec^{-1})*
0.013 Nm^{-2}	75 kJ	9.2×10^3
1.06 kNm^{-2}	92 kJ	9.5×10^5
1.2 kNm^{-2}	109 kJ	3.0×10^7
1.7 kNm^{-2}	113 kJ	1.6×10^8
2.6 kNm^{-2}	159 kJ	2.05×10^{14}

Both activation energies and frequency factors are strongly influenced by water vapour pressure, and show a stepped effect (Fig. 2).

The frequency factors given in Table 1 are very low at low partial pressures of water vapour. These low factors suggest[10] a transition state with very few degrees of freedom at low partial pressures, which gains additional degrees of freedom as the

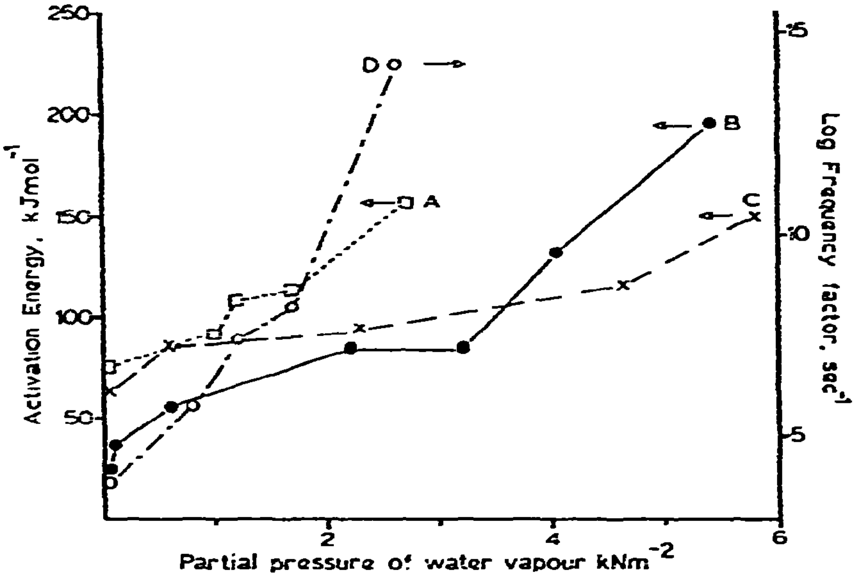

Fig. 2. Effect of partial pressure of water vapour on activation energy. A = This study (P.S.); B = β-CaSO$_4$ $\frac{1}{2}$H$_2$O^6; C = α-CaSO$_4$ $\frac{1}{2}$H$_2$O^7; D = frequency factor.

external vapour pressure rises. An alternative explanation is that, at low pressures, the reaction is surface-controlled, becoming bulk diffusion at higher pressures.

The activation energies derived for P.S. are higher than for the crystalline form[7] of $CaSO_4 \cdot \frac{1}{2}H_2O$ (the α-form) which range from 65 kJ at 0.013 Nm^{-2} to 98 kJ at 2.8 kNm^{-2}. These, combined with the lower frequency factors suggest that the higher peak maximum observed in the DTA studies is the consequence of kinetic rather than thermodynamic constraints.

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