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Investigation of phase transitions in the $\text{CaSO}_4(\text{s})\text{--H}_2\text{O}(\text{g})$ system by chromatographic methods

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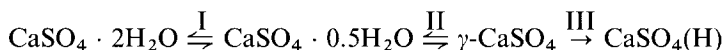
ABSTRACT

Modifications of chromatographic methods (differential flow and impulse) for investigating the kinetics and equilibrium of hydration and dehydration processes in the system $\text{CaSO}_4(\text{s})\text{--H}_2\text{O}(\text{g})$, and also for separately determining the hygroscopic and crystallization water (1.5 and 0.5 mol) of calcium sulphate, were developed. It is shown that the application of these methods permits complex investigations of the kinetics and equilibria of complicated heterogeneous processes to be carried out rapidly.

INTRODUCTION

One of the most promising trends in gas chromatography is its application to the investigation of physico-chemical processes in gas–condensed phase systems [1–4]. In this paper, which is a continuation of a series of investigations on heterogeneous reactions occurring with the gas phase present by chromatographic methods [5–8], the features and advantages of chromatographic methods for studying the kinetics and equilibria of phase transitions in the $\text{CaSO}_4(\text{s})\text{--H}_2\text{O}(\text{g})$ system are examined.

The redistribution of water in the system is a complicated topochemical process including reversible and irreversible macrostages according to the scheme



where $\gamma\text{-CaSO}_4$ and $\text{CaSO}_4(\text{H})$ are soluble and insoluble modifications of calcium sulphate, respectively.

The investigation of the equilibrium process of gypsum dehydration gives an opportunity to compare the results obtained by the chromatographic method with the literature data on the equilibrium under static conditions. The literature data on the kinetics of dehydration and rehydration processes are limited and contradictory. Further, the influence of inorganic acid additives on the nature of phase transitions in the system under examination was studied.

The investigation allowed the development of a rapid chromatographic method for the separate determination of the hygroscopic di- and hemihydrate water in the thermal treatment products of gypsum and phosphogypsum (multi-tonnage waste from phosphoric acid production).

EXPERIMENTAL

The reactor containing the specimen under study was connected to the flow of carrier gas of the gas chromatograph, the evolution and absorption of water vapour being registered by a thermal conductivity detector.

In a previous paper [8], it was shown that by varying the weight applied and the carrier gas velocity with no changes in the chromatographic installation, one can investigate both the kinetics and equilibria of chemical reactions. When investigating kinetics, the use of small weights permits the establishment of the conditions necessary for obtaining data in the kinetic region, where the slowing down of the process due to the withdrawal of gaseous products and the influence of thermal effects on the rate of the process are negligible. The kinetics of gaseous product evolution are registered simultaneously in the differential form (the height of the detector signal is directly proportional to the evolution rate of the volatile compound) and in the integral form (the degree of conversion is proportional to the area under the kinetic curve) [9].

In preliminary experiments conducted in order to establish the optimum conditions for correct kinetic data on gypsum dehydration, it was found that such kinetic conditions can be achieved with a weight of ≤ 0.1 g and a helium flow-rate ≥ 50 ml/min.

The transition to equilibrium dehydration conditions is attained by increasing the weight of the specimen tested to ≥ 5 g (with the layer $l = 50$ mm and $d = 3$ mm), saturation of the flow of carrier gas being provided by water vapour; the criterion for the equilibrium attained together with constancy of the detector signal is its independence of the contact conditions of water vapour with the condensed phase [a change in carrier gas velocity in the range 30–60 ml/min, dispersity ≥ 0.1 and ≤ 0.25 mm, mixing with the inert particles (melted quartz)].

When stepwise heating is used, a curve (Fig. 1) with step heights proportional to the equilibrium concentrations of water vapour above $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at each temper-

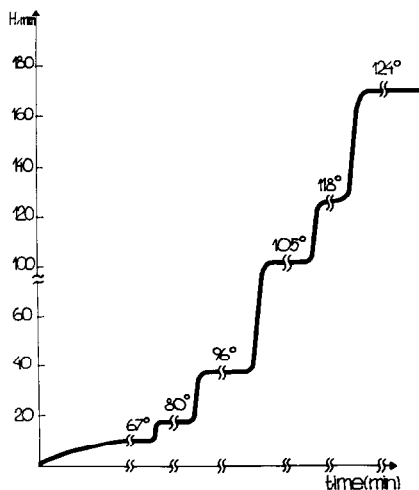


Fig. 1. Dependence of signal height (H) on temperature ($^{\circ}\text{C}$) in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

ature is obtained. Hence the dependence of the equilibrium water vapour pressure on temperature is determined in one experiment.

The impulse method, in which a water vapour zone of initially rectangular shape is moved through a layer of specimen by the flow of carrier gas, was used for studying the peculiarities of the $\gamma\text{-CaSO}_4$ and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ hydration process. Here the following variations in the contact phase conditions were applied: the layer of salt by changing the weight of salt in the range 0.1–1.0 g, a water dose value from $1 \cdot 10^{-3}$ to $300 \cdot 10^{-3}$ g, water vapour pressure in the impulse from 17.5 to 92.5 mmHg, helium flow-rate in the range 30–100 ml/min, contact times of 0.5–50 min and temperature in the range 20–60°C.

The water vapour zone of given concentration and amount was formed by introducing sufficient water with a liquid microsyringe onto thermostated inert layer of particles (melted quartz) ahead of the specimen; in special experiments it was shown that the formation of a zone of virtually rectangular shape in a flow of helium with an equilibrium water vapour concentration up to 70°C (Fig. 2, curve 1) is provided in such a microsaturator.

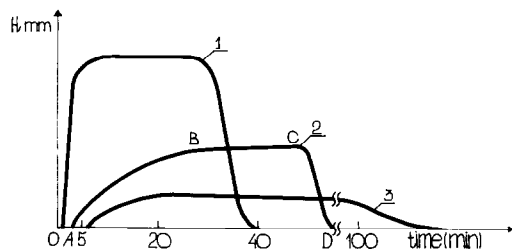


Fig. 2. Chromatograms of water evolution at 20°C: (1) quartz particles; (2) $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$; (3) $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} + 3\% \text{H}_3\text{PO}_4$.

As the phase transition kinetics in the system studied depend essentially on the legend of specimens (the method and conditions of synthesis), $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\gamma\text{-CaSO}_4$ were obtained directly in the experimental process by dehydrating primary $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under closely controlled conditions.

X-ray and IR spectrometric methods for analysis and the determination of specific surface areas were also used.

Pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and specimens with 2–5% of sulphuric or phosphoric acid added were used as primary materials.

RESULTS AND DISCUSSION

Fig. 3 shows the kinetic curves for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dehydration under isothermal conditions. Dissociation at a high rate starts at 70°C (0.1%/min) and proceeds intensively in the range 90–120°C in one macrostage. The maximum height of the kinetic curve is proportional to the maximum rate of the process. From the dependence of the maximum rate on temperature in the coordinates of the Arrhenius equation, the activation energy of the process is determined to be 83 kJ/mol. On the

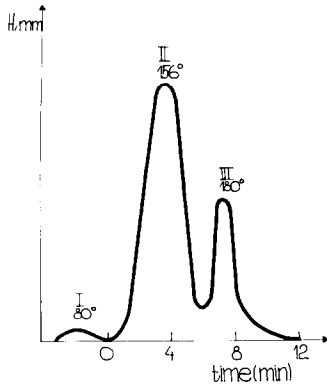


Fig. 3. Kinetic curves of dehydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under isothermal conditions. Sample weight, $5 \cdot 10^{-2}$ g; helium flow-rate, 60 ml/min.

basis of the kinetic data and X-ray and IR spectrometry it was established that $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ is not formed as an intermediate product under the kinetic conditions of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dissociation process. The dissociation is carried out up to the formation of $\gamma\text{-CaSO}_4$; the final product of the process is CaSO_4 (insoluble anhydrite), which is produced when $\gamma\text{-CaSO}_4$ is exposed to temperatures of 400–500°C for 1 h.

Fig. 4 shows the curves of water evolution when $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with 3% of sulphuric acid added are heated, the heating rate of the specimens being 10°C/min; under these conditions the dehydration is realized in the intermediate regime, which promotes splitting of the process into macrostages. As can be seen, the introduction of the acid significantly influences the kinetics of the dehydration process, the phase transition temperatures decreasing and the dehydration rate increasing, but the splitting of the process into stages becomes worse. The temperature of the $\gamma\text{-CaSO}_4$ transition into insoluble CaSO_4 also decreases, although the latter can be obtained when the specimen is maintained at 120°C for 30 min. Such a change in the kinetic characteristics is connected with a change in the mechanism of the de-

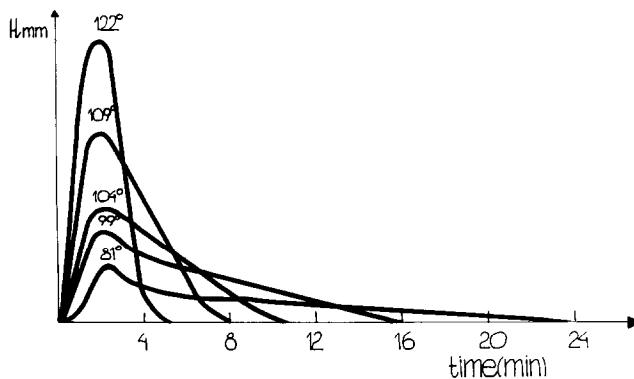


Fig. 4. Curves for dehydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Sample weight, 1 g; heating rate of specimen, 10°C/min.

hydration process as a result of the dehydrating influence of sulphuric acid. The correlation of the equilibrium water vapour pressures above the concentrated sulphuric acid solutions and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ shows that the dehydration in the presence of sulphuric acid occurs through the formation of a solution film on the surface of particles and its evaporation. A similar, but less intensive, influence is exercised by phosphoric acid.

A stepwise chromatogram illustrating the dehydration of calcium sulphate hydrates under the equilibrium conditions is presented in Fig. 5. The heights of steps I and II are proportional to the equilibrium water vapour concentrations above $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, respectively. The ΔH value for $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ dehydration is found to 63 kJ/mol, which agrees satisfactorily with that in the literature [10].

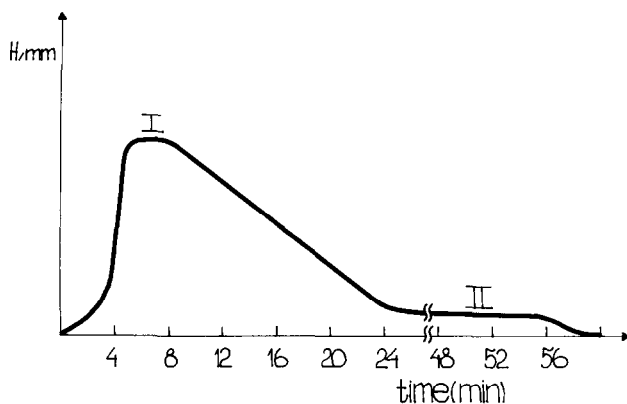


Fig. 5. Curves for dehydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under equilibrium conditions at 87°C . Sample weight, 10 g.

The investigation of hydration by the impulse method showed that $\gamma\text{-CaSO}_4$ hydration with the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ is a very rapid process. When the water vapour impulses are moving, quantitative water absorption (without a skip) takes place and also layer by layer movement of the front edge of the reaction zone up to the complete conversion of the entire specimen into $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$; hence the reaction rate is significantly greater than that of the water vapour impulse movement. The hydration of freshly prepared $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ with the formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is relatively slow. In the temperature range $18\text{--}30^\circ\text{C}$, water vapour pressure range $17\text{--}30$ mmHg and with a contact time of less than 10 min, a change is observed only in the shape of the zone (Fig. 2, curve 2) compared with the primary one (Fig. 2, curve 1). When the temperature is increased to $45\text{--}50^\circ\text{C}$, the water vapour pressure to 92.5 mmHg and the contact time to over 60 min, partial water absorption from the impulse is initiated together with the formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which reached 15% at 50°C and an impulse movement time of 180 min. For specimens containing 3% of phosphoric acid, the formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under the above conditions did not occur, *i.e.*, the slowing down influence of the acid additions on the hydration process is observed.

From the comparison of the curves in Figs. 2 and 3, it is clear that a change in the zone shape is taking place when the water vapour zone moves through the specimen $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. As can be seen, for pure $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ broadening of the front zone alone (section BC of curve 2) is observed; for the specimen with phosphoric acid added, the broadening of both the rear and the front edges of the zone is observed (Fig. 2, curve 3). It may be considered that the change observed in the shape of the elution curve is characteristic of the water vapour reversible sorption process, hence the difference in curves 2 and 3 seems to reflect a change in the mechanism of the hydration process.

The investigations conducted have allowed the establishment of the optimum conditions for splitting of the process into stages, corresponding to the evolution of hygroscopic water and crystallization water (1.5 and 0.5 mol) and the development of a chromatographic method for determining the forms of water present in the products obtained when gypsum and phosphogypsum are dried. The method is rapid (a determination requires 30–40 min) and is suitable for the determination of the crystallohydratic composition of specimens. The error is 5%.

The investigations performed on hydration and dehydration in the $\text{CaSO}_4(\text{s})\text{--H}_2\text{O}(\text{g})$ system show the advantages of the use of gas chromatographic methods for complex studies of heterogeneous chemical reactions with the gaseous phase present.

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