

Formation of super disperse phase and its influence on equilibrium and thermodynamics of thermal dehydration

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Abstract

New data on the dehydration and rehydration processes of calcium, manganese and copper dichlorides are presented that reveal surprising, in a certain sense, behaviour difficult to be explained for the last two chlorides in terms of the usual conception of thermodynamic equilibrium. A substantial role of a super disperse phase at studying the equilibrium of the thermal decomposition of a hydrate is postulated to explain the experimental results for manganese and copper dichlorides. It is shown that the formation of such a phase of the hydrate is able to change appreciably the experimental results, causing the increase of water vapour pressure and the decrease of the derived enthalpy of a reaction. The results obtained allow to understand the reasons for considerable differences of some literature data. They enable to receive more precise and reliable data for thermal dehydration and probably for some other decomposition processes.

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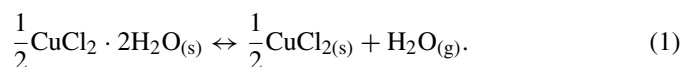
1. Introduction

In a detailed and comprehensive analysis of numerous existing data on thermal dehydration of crystalline solids Galwey [1] introduced and developed new approaches for understanding the nature of this important group of heterogeneous reactions. Great attention was paid to the structural changes and mechanisms of interfacial processes and their influence on the thermal dehydration kinetics; but the problems of equilibrium and thermodynamics have not been practically touched.

Do these interfacial processes have any relation to equilibrium and the received thermodynamic properties of the reactants? At first sight they do not, as equilibrium is a stable state of a system, not depending on its history and the rate of equilibration. That is, the results of a thermodynamic study of thermal dehydration should not be influenced by any peculiarities of its mechanism – all the participating phases should have their equilibrium structure, and the system should be characterized by the minimum of the Gibbs energy.

Such an approach is theoretically absolutely correct, except for the two obvious and important circumstances. The first, the reality is that the experiment cannot continue infinitely long, and the second, the process of equilibration may proceed very slowly. Therefore, in practice we encounter very often a quasi-equilibrium state of a system, which is not always easy to distinguish from the true equilibrium. Thus, there is no simple and definite reply to the above-asked question.

In this paper, we present the experimental results on the dehydration and rehydration processes of calcium, manganese and copper dichloride hydrates. The data obtained for the last two chlorides permit us to suppose a substantial role of the interfacial processes in special cases of the thermodynamic investigations of thermal dehydration. The choice of these substances was not accidental – all of them have a rather high desiccating ability, anhydrous CaCl_2 is widely used in industry and laboratories; MnCl_2 is a promising desiccant, and CuCl_2 was recently shown [2,3] to be a desiccant with a very low temperature of regeneration:



The latter chloride has an important peculiar property – it forms the only one hydrate stable at ordinary conditions, the

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dihydrate. Therefore, in this case we may expect the easiest interpretation of the experimental results. Indeed, the most conclusive proof on the problem concerned was received for this chloride in particular.

2. Experimental

2.1. Chemicals

All used chemicals were of analytical or chemical grade purity. Anhydrous CaCl_2 and MnCl_2 were obtained by careful and stepped heating of the recrystallized hydrates in the oven up to the temperature 520 K. Special attention was paid to prepare pure $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, since there are many differences in literature concerning its characteristics. This hydrate was prepared by double recrystallization of a commercial sample from hot water, slightly acidified with HCl. The crystals were washed with cold water on a glass filter and dried in air; they form small blue needle-like crystals. They are noticeably hygroscopic, probably due to the adsorption of water vapour on the surface of the crystals. Anhydrous CuCl_2 was obtained by heating the hydrate in the oven at the temperature 390 K. All the concerned anhydrous salts are strongly hygroscopic.

2.2. Experimental procedure

In order to reveal the desired information, the experimental methods should be used allowing to receive not only the equilibrium knowledge but also some features of the dynamics of the concerned process. Therefore, two methods of this kind were chosen to measure the equilibrium water vapour pressure for the systems, including the anhydrous salts and their lowest hydrates.

The first one was the gas transpiration technique. A schematic diagram of the arrangement used is shown in Fig. 1. The flow of nitrogen was passed through a filter bed of the chloride and its hydrate (Fig. 2), and the partial water pressure at the outlet of the apparatus was found gravimetrically.

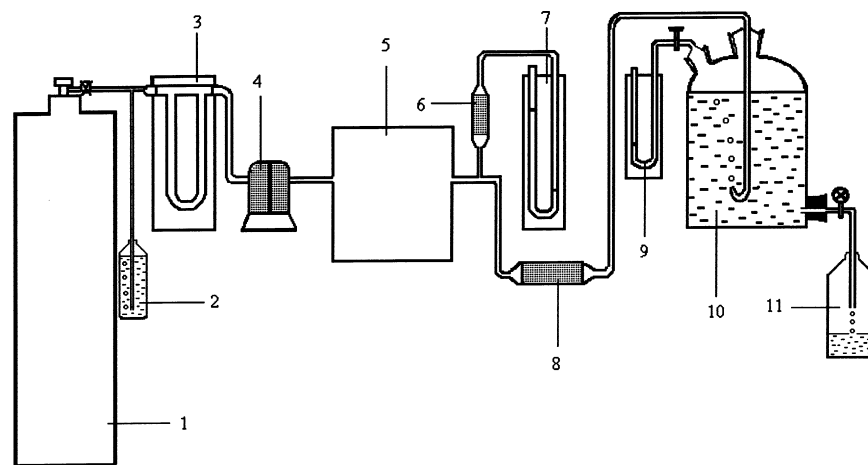


Fig. 1. Schematic diagram of the arrangement for the gas transpiration technique: 1, nitrogen cylinder; 2, manostat; 3, capillary rheometer; 4, CaCl_2 or water saturator in a Dewar; 5, saturation block; 6, CaCl_2 protection; 7, large water manometer; 8, weighed absorption vessel; 9, small water manometer; 10, large bottle to collect nitrogen; 11, bottle to collect water.

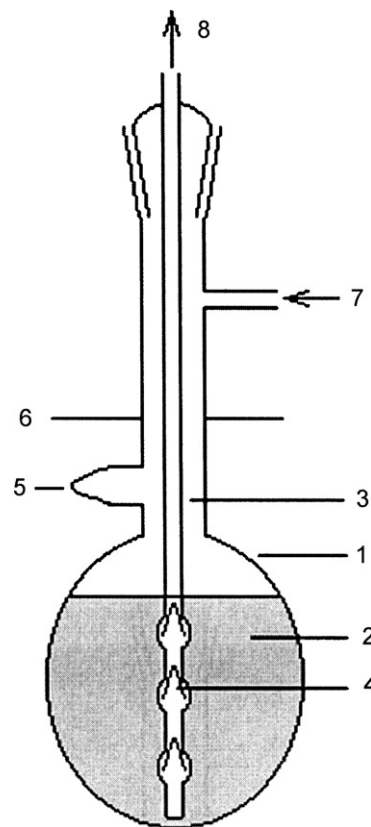


Fig. 2. Reaction vessel for the gas transpiration technique: 1, pyrex glass flask; 2, substance; 3, inner glass tube to withdraw gas; 4, glass fiber filter; 5, sealed off tube for loading substance; 6, water level in thermostat; 7, gas supply; 8, gas outlet.

A special procedure was used to prepare granulated chlorides applied on the surface of silica gel. Silica gel was ignited in the oven for 10 h at 1270 K to produce 1–2 mm granules with closed porosity. It was denoted by the considerable growth of bulk density, from 0.41 g cm^{-3} for the initial silica gel reduced to the similar particle size, to 1.28 g cm^{-3} for the ignited product. The specific water vapour sorption was determined gravimetrically

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