Thermal stability and thermodynamics of manganese(II) chloride monohydrate

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ABSTRACT

Three tensimetric methods were used to measure the equilibrium water vapour pressure for the reaction $MnCl_2 \cdot H_2O(s) = MnCl_2(s) + H_2O(g)$ over the temperature range (353.25 to 500.3) K. Two additional effects were considered, viz. possibility of a hydrate super disperse phase formation and probability of manganese(II) chloride hydrolysis with water vapour. A linear equation was derived for the temperature dependence of the water vapour pressure: $\ln(p/p^\circ) = 14.981 - 7517 \cdot (K/T)$. The standard enthalpy and entropy of this process were calculated at the mean temperature 425 K: $\Delta_r H^\circ (425) = (62{,}500 \pm 200)$ J, $\Delta_r S^\circ (425) = (124.56 \pm 0.47)$ J $\cdot$ K^{-1}. At the standard temperature these quantities were calculated using the approximate constant value of $\Delta_r C_P^\circ = (-8.3 \pm 2)$ J $\cdot$ K$^{-1} \cdot$ mol^{-1}: $\Delta_r H^\circ (298) = (63{,}550 \pm 500)$ J, $\Delta_r S (298) = (127.5 \pm 1.2)$ J $\cdot$ K^{-1}. Standard thermodynamic characteristics of manganese(II) chloride monohydrate were obtained: $\Delta_f H_m^\circ (298) MnCl_2 \cdot H_2O(s) = (-786.6 \pm 0.9)$ kJ $\cdot$ mol^{-1}; $S_m^\circ (298) MnCl_2 \cdot H_2O(s) = (179.5 \pm 1.6)$ J $\cdot$ K$^{-1} \cdot$ mol^{-1}.

1. Introduction

It was noted recently that some anhydrous salts may reveal promising desiccating ability for drying different gases [1], and if necessary assure mild conditions of drying. It is important that the equilibrium water vapour pressure in the systems formed with anhydrous salts and their lowest hydrates does not depend on the degree of sorption. Very many salt systems with various characteristics are available; some of them may be used to dry such chemically active gases as hydrogen chloride, hydrogen fluoride, chlorine and others. Therefore thorough investigations of their lowest hydrates formation, thermal stability and thermodynamics are necessary.

Manganese(II) chloride is one of such promising dryers, and in accordance with some preliminary thermodynamic calculations its desiccating ability might exceed that for the widely used calcium chloride. However, our gas transpiration experiments [2] have not proved it to be true, and the reason for that was advanced, consisting in possible formation of a metastable super disperse phase of the hydrate. In addition, different thermodynamic sources give very differing results, as may be seen in figure 5. Hence, a tensimetric reinvestigation of thermal stability and thermodynamics of the lowest manganese(II) chloride hydrate was undertaken. Two additional effects were considered: firstly, the above-mentioned possibility of the hydrate super disperse phase formation, and

secondly, probability of manganese(II) chloride hydrolysis with water vapour.

2. Experimental

The initial hydrate $MnCl_2 \cdot 4H_2O$ was somewhat contaminated with its oxidation products though it was of analytical grade purity. It was dissolved in distilled water, filtered and crystallized at room temperature from the solution acidified with HCl after some water was evaporated. The crystals were washed with cold water on a glass filter and dried in a box with anhydrous $CaCl_2$ as long as a free-flowing product was obtained.

It was analyzed for metal and chlorine using the special precise standards; the uncertainty of their composition did not exceed ±0.1%. As a result, the stoichiometric composition of the tetrahydrate was determined to be $MnCl_{2.001 \pm 0.010} \cdot (4.03 \pm 0.04)$ H_2O. Water content was also received by drying the tetrahydrate from the amount of the evolved water and the initial mass of the substance – $MnCl_2 \cdot (3.997 \pm 0.004)$ H_2O.

The lowest hydrate $MnCl_2 \cdot H_2O$ was prepared by careful heating the tetrahydrate in an oven, initially at the temperature 325 K to avoid melting, and then at 395 K. Its stoichiometric composition received by drying to the anhydrous salt was $MnCl_2 \cdot (1.000 \pm 0.001)$ H_2O. Another convenient method for the synthesis is to heat the tetrahydrate in vacuum at temperatures up to 373 K, since at this temperature the monohydrate loses water very slowly.

The system $(MnCl_2 + H_2O)$ was studied derivatographically (DTA technique) using the Paulik–Paulik–Erdey Q-Derivatograph and a special Pyrex glass ampoule with a thin capillary, strongly

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reducing the rate of the gas diffusion from inside and outside [1]. Thus we could measure "boiling temperatures" at the atmospheric pressure. Different heating rates (4.5, 2.3, 1.3, and 0.7) $K \cdot min^{-1}$ were used in order to reveal slow processes, and extrapolation to the zero rate was made in case of need. The sample mass was (0.26 to 0.38) g. The Pt–Pt/Rh thermocouple of the derivatograph was calibrated using precise thermometers, melting temperatures of ice and pure metals, as well as boiling temperatures of water and pure organic liquids. The resulting uncertainty of the temperature measurements was obtained to be ±0.8 K.

Water vapour pressure for the process

$$MnCl_2 \cdot H_2O(s) = MnCl_2(s) + H_2O(g) \qquad (1)$$
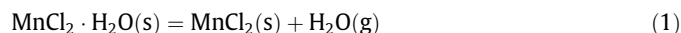
was measured using three tensimetric methods: the static method with a glass membrane null-manometer of Novikov and Suvorov [3], the dynamic gas transpiration and "boiling temperature" methods, which were all described earlier [1,2].

Specific surface area of the sample ($MnCl_2 \cdot H_2O + MnCl_2$), obtained from the null-manometer chamber after the tensimetric experiment, was measured with the method of low temperature adsorption of argon [4].

3. Results and discussion

Preliminary information concerning the manganese(II) chloride stability with respect to the hydrolysis reaction was received in special experiments with its tetrahydrate stepped dehydration. A sample of $MnCl_2 \cdot 4H_2O$ (m = 30.72 g) was heated for 1 h in vacuum about 1 hPa in a water bath. Water vapour together with a small amount of hydrogen chloride was condensed in a glass trap cooled with liquid nitrogen, the condensate mass was found by weighing the trap after the experiment to ±0.01 g. It allowed calculation of the composition of the residual hydrate. The hydrogen chloride amount was found by alkaline titration of the unfrozen solution, and the fractional conversion of eliminated water was thus obtained on the assumption that one water mole produced one hydrogen chloride mole. It was equal to 0.002% at T = (325 to 345) K (the residual hydrate contained n = 1.7 mole H_2O per mole of the chloride), and to 0.04% (n = 1.0 mole H_2O) at the temperatures up to 373 K. Further dehydration to the anhydrous salt was found to be very slow, so it was carried out at the atmospheric pressure in a tube in stream of dry nitrogen for 15 h (m = 4.6506 g) at T = (420 to 470) K. In this most interesting case, the fractional conversion of eliminated water was found to be 0.4%. Thus these experiments indicate a quite real though moderate influence of the hydrolysis reaction on the results of tensimetric study of process (1).

A typical derivatogram of the tetrahydrate $MnCl_2 \cdot 4H_2O$ (m = 0.2769 g) is shown in figure 1. Four peaks are observed in this figure in accordance with the results provided in reference [5].

1. Incongruent melting of the tetrahydrate with the formation of the solid dihydrate and the saturated solution, no mass loss due to water evaporation is observed at this stage. This process is non-variant; therefore its temperature should not depend upon pressure. Such is the case indeed, the temperature found (328.9 K) is in fair agreement with the results of [5] (328.2 K) and the solubility diagram of manganese(II) chloride in water [6] (331.3 K). This temperature does not depend upon the heating rate except for the highest one (4.5 $K \cdot min^{-1}$). It agrees with the results for pure water and copper(II) chloride dihydrate [1] and confirms the rule that in our conditions this heating rate provides only general and preliminary results.
2. Water evaporation from the saturated solution in presence of the solid dihydrate. To our surprise, the observed boiling tem-
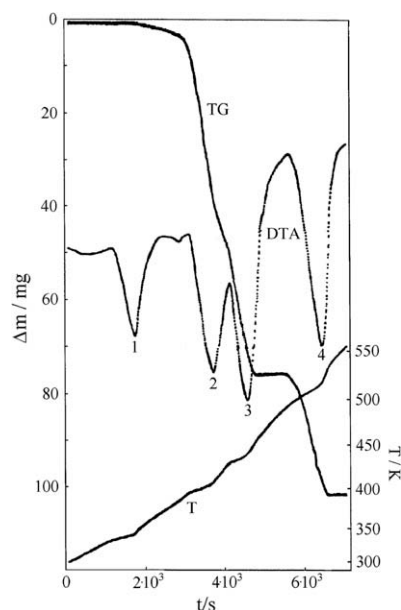

FIGURE 1. Typical derivatogram of $MnCl_2 \cdot 4H_2O$ (heating rate 4.5 $K \cdot min^{-1}$).

perature revealed obvious dependence on the heating rate V (T/K = 389.7 + 1.254 · V), probably due to the surface over saturation at water evaporation. Our extrapolated value T = 389.7 K substantially exceeds the result of [5] (375.2 K). The reason for that is discussed below (figure 2).

3. Thermal decomposition of the dihydrate and the monohydrate formation, the observed "boiling temperature" 416.4 K is also higher as compared with 408.2 K [5].
4. Thermal decomposition of the monohydrate to anhydrous $MnCl_2$. The observed "boiling temperature" is 500.3 K and once again considerably exceeds the result of [5] (483.2 K).

It is seen in figure 1 that the intermediate dihydrate is only slightly stable, whereas the lowest (monohydrate) has a rather wide temperature range of stability. Therefore synthesis of the exactly stoichiometric monohydrate becomes possible as stated above.

In figure 2 temperature dependence of water vapour pressure is shown for all monovariant processes including three manganese(II) chloride hydrates.
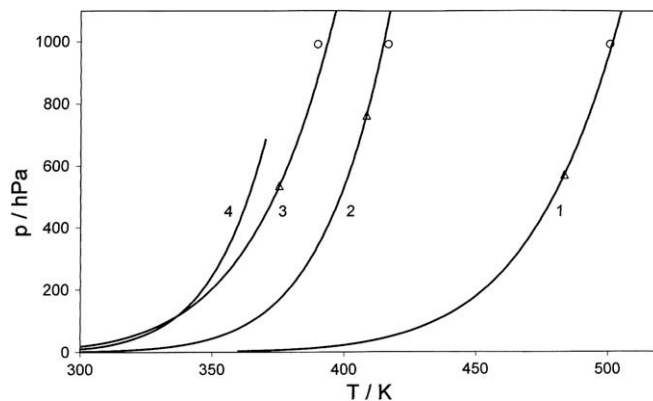

FIGURE 2. Plot of water vapour pressure against temperature for all process including manganese(II) chloride hydrates. ○ – our DTA results at p = 991.9 hPa; △ – work [5].