



## Methodology for experimental determination of equilibrium water vapor pressure in magnesium chloride hydrates

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### Abstract

Thermochemical energy storage (TCES) based on the reversible reaction of salt hydrates is a promising heat storage technology due to its high energy density and negligible long-term heat losses. A key parameter in TCES is the equilibrium water vapor pressure, which determines the direction of hydration and dehydration reactions under given conditions. Although the Clausius-Clapeyron relation provides a theoretical description of equilibrium conditions, experimental validation is required. This work describes an experimental method for determining the equilibrium water vapor pressure of salt hydrates using absolute pressure measurements. The method was applied to investigate the reversible reaction  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$ . Equilibrium pressure versus temperature curves were obtained over the temperature range of 35–70°C. Measurements were performed on four independent samples to verify repeatability. The results show high consistency and good agreement with the literature data.

**Keywords:** equilibrium pressure, salt hydrates, thermochemical energy storage, water vapor

### 1. Introduction

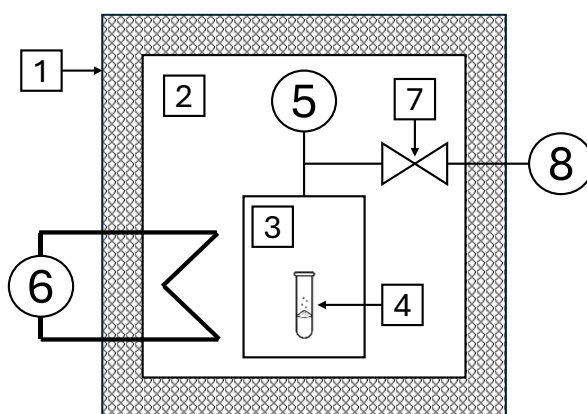
The field of thermal energy storage technology has become increasingly popular in the past few years. In particular, research into thermochemical energy storage (TCES) has gained significant attention, as it is currently the most promising heat storage method. TCES offers many advantages, including high energy storage density and the potential for long-term storage without heat losses. This technology is based on reversible chemical reactions that involve significant heat effects. In the reaction bed of the TCES unit, the endothermic reaction occurs during charging, whereas the exothermic reaction occurs during discharging. For low-temperature TCES applications, salt hydration reactions are frequently reported in the literature as promising candidates. Examples of salt hydrates that are considered as potential thermochemical materials include:  $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  [1-3]. The TCES based on salt hydrates uses the reaction of salt hydration during discharging and the reaction of dehydration during charging. One of the most important parameters of thermochemical materials is the equilibrium water vapor pressure over them at a given temperature. When the water vapor pressure above the salt exceeds the equilibrium pressure, the exothermic hydration process begins. Conversely, when the water vapor pressure is lower than the equilibrium pressure, endothermic dehydration occurs. The equilibrium water vapour pressure over the salt hydrates is strictly connected to the temperature, as described by the Clausius-Clapeyron equation [4]. Nevertheless, the Clausius-Clapeyron equation requires detailed data on the enthalpy and entropy of the reaction at a given temperature. Moreover, the Clausius-Clapeyron relation is valid only when distinct pure phases are present, which is not always the case, as metastable forms of hydrates may coexist during TCES operation. Microstructural effects and mass transfer limitations could also potentially influence the apparent equilibrium. Therefore, experimental data are needed to confirm the predictions of the Clausius-Clapeyron model.

This study focuses on the methodology for determining the water vapor equilibrium pressure in the presence of salt hydrates. The experiment is based on absolute vapor pressure measurements, as

described in the literature [5]. The proposed experimental setup is modified from the one described in the literature [5] to enhance heat transfer and, consequently, accelerate the stabilization of temperature and pressure to equilibrium conditions. The developed experimental setup was used to measure the equilibrium pressure vs temperature curve for the reversible reaction  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$ .

## 2. Methodology of equilibrium pressure measurement

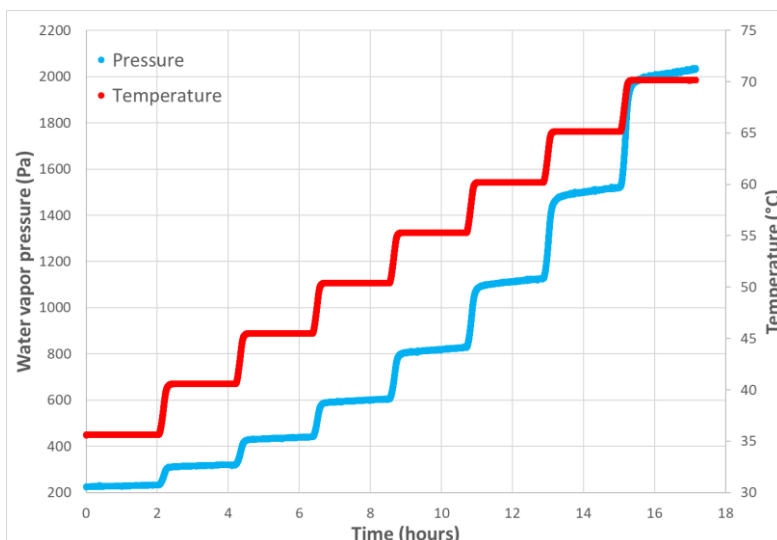
The experiment presented in this paper is based on a similar experiment and measurements published in the literature [5]. The core of the method is to measure the absolute pressure of water vapor, which is released from the hydrate under vacuum conditions. The schematic diagram of the experimental setup used in this work is shown in Fig. 1.



**Fig. 1** Schematic diagram of the experimental setup for measuring the pressure vs. temperature equilibrium curve, where: 1 – thermal insulation, 2 – thermostatic chamber, 3 – measurement vessel, 4 – salt hydrate sample, 5 – pressure and temperature sensor, 6 – temperature control unit, 7 – cut-off valve, 8 – vacuum pump.

The measurement procedure begins with preparing the salt hydrate sample. First, the hydrated form of salt is placed in the small test tube. The sample mass is small and typically does not exceed 1 g. The salt hydrate is then placed inside the measurement vessel. In the developed experimental setup, the vessel is a short copper tube connected to the pressure-temperature sensor and the cut-off valve. The sensor used to measure absolute pressure is a Keller PAA-33X with a range of 0-0.3 bar abs, which also measures temperature. All connections between the copper tube, sensor, and cut-off valve are SAE flare fittings, which are known for use in both high-pressure conditions and under vacuum applications. When the sample is placed inside the copper tube, the tube is sealed, the ball valve is opened, and the vessel is evacuated using the vacuum pump. The evacuation lasts 45 minutes, during which the salt hydrate sample dehydrates. This process occurs because a vacuum is created around the hydrate, lowering the local water vapor pressure below the equilibrium pressure at ambient temperature. As a result, the sample consists of the hydrated form of salt that was placed in the tube test, along with the less hydrated salt formed during the evacuation of the measurement vessel. After 45 minutes of evacuation, the cut-off valve is closed, and the vessel is placed inside the thermostatic chamber, which is maintained at a constant temperature of 35°C. The chamber is filled with circulating dielectric oil to accelerate heat transfer and, consequently, reach equilibrium more quickly. The temperature of the circulating oil is maintained by the Huber temperature control unit. The oil container is insulated with ArmaFlex to maintain a constant temperature inside. The main measurement begins after 15 minutes, by which time the temperature inside the measurement vessel will have reached 35°C. The absolute pressure inside the vessel is measured every two seconds, while the temperature is held constant for two hours. It is assumed that the measured absolute pressure is due to water vapor and that no other gases are present in the measurement vessel. After two hours, the Huber temperature setpoint is changed to achieve the next equilibrium state at a higher temperature. The heating rate is 0.5°C/min and lasts 10 minutes. The temperature is then held constant for the next two hours. This sequence continues until the equilibrium

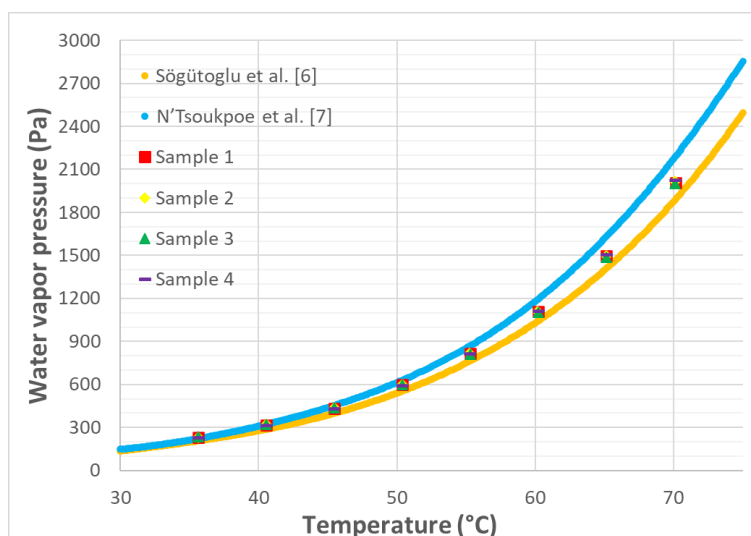
pressure is measured at a temperature of 70°C. A single experimental run lasts 17 hours and 10 minutes, and 8 different equilibrium states are measured. The complete course of the experiment for one sample of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is presented in Fig. 2.



**Fig. 2** The course of equilibrium pressure measurement for the reaction  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$ .

### 3. Results

The experimental setup was used to measure the equilibrium water vapor pressure for the reaction  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$ . To confirm the repeatability of the results at the preliminary stage of the research, four different samples of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  were studied. All measurements were divided into 8 segments, and temperature variation within each segment during measurements was maintained at less than 0.01°C. The mean absolute pressure measured at each segment was treated as the equilibrium pressure of water vapor at a given temperature. The results for all samples were very similar. The greatest difference was observed between samples 3 and 4 at the temperature of 70°C, with an equilibrium pressure difference of 24.7 Pa. The results for all samples, compared with the literature data [6, 7] are presented in Fig. 3.



**Fig. 3** Measurement results for the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$  reaction compared with the equilibrium pressure vs temperature curves reported in the literature [6, 7].



#### 4. Conclusions

The work focuses on the methodology for determining the equilibrium water vapor pressure in the presence of salt hydrates. The experiment is based on absolute vapor pressure measurements. The experimental setup was developed, and initial tests were conducted to confirm the reliability of the measurement method. Four samples of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  were measured to determine the equilibrium water vapor pressure for the reversible reaction  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$ . The results obtained are consistent with the literature data. The measurement results appear to be repeatable and reliable, but to confirm them, additional samples and a wider variety of salts need to be investigated.

#### Acknowledgements

This work was financially supported by the National Science Centre (Poland) within the Project No. 2020/37/B/ST8/04021.

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