



# A review of salt hydrates for seasonal heat storage in domestic applications



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## HIGHLIGHTS

- We report an evaluation of potential hydrate reactions for heat storage application.
- Thermodynamic data of almost 600 hydrate reactions are collected.
- A shortlist of 25 TCM hydrate reactions is identified based on thermodynamic data.
- Salt hydrates as seasonal heat storage is not realistic for large scale implementation.

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## ABSTRACT

A literature review is performed in order to collect and analyse the thermodynamic data of an utmost number of salt hydrate reactions (i.e., 563 reactions are reviewed). These data allow us to evaluate the theoretical possibilities and limitations of salt hydrates as thermochemical materials (TCMs) for seasonal heat storage in the built environment (1 GJ/m<sup>3</sup> on system level). Two filters are used for evaluation. Filter 1 including three criteria i.e., an ideal hydration reaction with a capacity larger than 2 GJ/m<sup>3</sup>, a hydration temperature of 65 °C (suitable for domestic hot water) or higher, a dehydration temperature below 100 °C to profit as much as possible from the solar heat that can be harvested. Only four of the studied hydrates fit with these demands. For selecting a larger number of hydrates, a second filter is introduced with less demanding constraints. It is expected that modifications on heat storage system level are needed to reach an acceptable system performance with the hydrates selected through filter 2 (hydration reaction with a capacity larger than 1.3 GJ/m<sup>3</sup>, a hydration temperature of 50 °C or higher, a dehydration temperature below 120 °C). Based on this filter, a shortlist of 25 TCM hydrate reactions are identified, including the four of filter 1. The shortlist is analyzed by considering price, chemical stability, reaction kinetics and safety for domestic environment. Based on this additional analysis with the used constraints, K<sub>2</sub>CO<sub>3</sub> is determined to be the most promising candidate for open or closed systems, but has a low energy density. Based on the review of 563 hydrate reactions, we concluded that no ideal salt exists for seasonal heat storage under the considered boundary conditions. With the current concept of seasonal heat storage, including closed and open systems, whereby only one dehydration cycle per year is performed under a system energy density of 1 GJ/m<sup>3</sup>, it is not realistic for large scale implementation to use pure salt hydrates as heat storage material. By adjusting the constraints, such as multiple cycles per year or higher water vapor pressures, salt hydrates can still be used as TCMs. It should be mentioned that MgSO<sub>4</sub>·7H<sub>2</sub>O, MgSO<sub>4</sub>·6H<sub>2</sub>O and CaCl<sub>2</sub>·6H<sub>2</sub>O are not listed in our shortlist of 25 TCMs, although these hydrates are commonly suggested in the literature as promising TCM for seasonal heat storage. The present study on *pT*-characteristics shows, however, that these salts are not fitting the demands of such a heat storage system.

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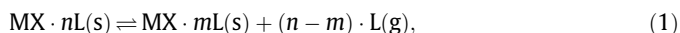
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## 1. Introduction

### 1.1. Heat storage

Currently society is moving from carbon-based to more renewable energy sources in order to become less dependent on fossil fuels. A dominant part of the energy consumption of European residential sector (around 70% of the total consumption [1]) is related to domestic space heating and hot tap water generation. A cleaner sourcing of this part of the energy sector will have a large impact on the carbon production. For generation of carbon-free heat, new energy production techniques must be implemented, the majority of which are based on capturing solar radiation. However, solar radiation fluctuates on different time scales, i.e., hourly, daily and seasonally. The power generated fluctuates, resulting in a variable and unpredictable supply of heat. For matching heat demand and supply, heat storage systems that account for the timescale of radiation fluctuations are required.

In this article, the focus is on seasonal storage in the built environment in the future, requiring a storage capacity of about 7–12 GJ in a typical West European dwelling based on the passive house standard (<http://www.passivehouse.com/>). This storage capacity is based on an average dwelling in the Netherlands with a floor area of 120 m<sup>2</sup>, with the passive house standard of 15 kWh/m<sup>2</sup> for newly built houses and 28 kWh/m<sup>2</sup> in renovated houses [2,3]. A promising heat storage concept is based on a thermochemical reaction, which was suggested by Goldstein [4] in the sixties and gained interest in the last decade [5–7]. The solid materials involved in these reactions are called thermochemical materials (TCMs). Key advantages with respect to techniques like sensible heat storage and phase change materials (PCM) include nearly loss-free storage period and high energy density. In general, a gas-solid equilibrium reaction can be represented by:



wherein  $MX \cdot nL(s)$  is a solid salt complex consisting of a salt  $MX \cdot mL(s)$  and  $(n-m)$  mol of reactive gas  $L$ . In the current literature reactive gas  $L$  is considered to be  $H_2O$ ,  $NH_3$  or  $CH_3OH$ . As the targeted heat storage system should be used in residential areas,  $NH_3$  and  $CH_3OH$  are not considered because of currently strict Dutch safety regulation [8]. As a result,  $H_2O$  is considered a reactive gas in this article.

The amount of reactive gas  $L$  inside salt complex  $MX$  is called the loading of the salt. The formation reaction of  $MX \cdot nL$  is exothermic, i.e. it produces energy what can be used when for heating purposes. The enthalpy of this formation reaction is  $\Delta_r H_{m \rightarrow n} \equiv \sum_{\text{reactant}} \Delta H_i - \sum_{\text{products}} \Delta H_i < 0$ . The reverse decomposition reaction of  $MX \cdot nL$  is endothermic,  $\Delta_r H_{n \rightarrow m} = -\Delta_r H_{m \rightarrow n}$  thus costs energy. This happens during summer heat storage periods. The equilibrium reaction in Eq. (1) implies that the maximum loading of a salt  $MX$  at a temperature  $T$  is determined by the vapor pressure of  $L(g)$ .

### 1.2. Aim

During the past decade, many researchers have investigated TCM's as heat storage materials. The first generation of salt hydrates based on TCMs have already been developed, varying from lab-scale [9–11] to field demonstrations [12–14]. A complete overview of the systems constructed in the last decade is given by Scapino et al. [6]. A great body of research is also available on high potential salts for temperature storage below 100 °C, such as  $MgSO_4$  [15–19],  $MgCl_2$  [19–22],  $SrBr_2$  [7,23],  $Na_2S$  [12,24] and  $CaCl_2$  [22,25,26] which have been studied in detail. Storage of heat for temperature applications between 100 and 300 °C already shows some promising results with salts based on  $CaO/Ca(OH)_2$  [27] and  $CaC_2O_4/CaC_2O_4 \cdot H_2O$  [28]. Furthermore, some reviews have been published on TCM's [5,29–34], that use the energy density as selection criterion, with one exception focusing on applied working conditions [5] during hydration/dehydration. In the latter study three salts were selected:  $MgSO_4$ ,  $LaCl_3$  and  $SrBr_2$  based on dehydration below 105 °C and rehydration at 20 mbar vapor pressure at 25 °C, which corresponds to the saturated vapor pressure in equilibrium with a water reservoir at 17 °C. However, the missing parameter for selection in this review is the generated temperature  $T_h$  during the hydration reaction, since this temperature is the highest output temperature the heat battery can deliver.

For introduction of TCMs on the market, it is important that TCMs are able to match the demands of the customers. As a first indication it is therefore necessary to determine if TCMs can theoretically match such demands. In the present work, we attempted to analyze and extend the search for pressure-temperature ( $pT$ ) data on the basis of demanded working conditions of a TCM reactor in the built environment, i.e. a system that can store 10 GJ, deliver

hot tap water at 65 °C and can be charged in summer with the help of solar panels. The goal is to select TCM's which fulfill the temperature demand and energy density of the consumer, with the help of available  $pT$  data, and analyse the plausibility of using these TCM's. Firstly, the process of data collection will be summarized, secondly the selection criteria are explained. Based on these criteria a short list of the most promising salts will be generated and discussed in view of the target application.

## 2. System description

Since a heat storage of approximate 10 GJ stored heat is needed to overcome seasonal fluctuations [35], a system level energy density of 1 GJ/m<sup>3</sup> is considered in this paper, meaning that 10 m<sup>3</sup> of reactor should be placed in housing. The system energy density (considering the entire installation, including TCM material, piping, valves, control devices) is based on the energy density of 5 times the energy density of a water tank by a  $\Delta T$  of 50 °C. Ten cubic meters of reactor is probably still an overestimation of the available space for such a system as the space is limited i.e. apartments.

In Fig. 1 the concept of a heat storage system with help of a TCM is schematically given. On the top, the reactor system is shown, where two compartments are drawn, one filled with a TCM and the other with water, in between these compartments a valve is located.

For heat storage, two main concepts are considered, closed and open systems [7]. In the case of a closed system both compartments are part of the system and all water necessary for the hydration/dehydration reactions is stored within the system. In the case of an open system, the water is not stored in the system itself, but

externally released/supplied to the system dependent on TCM dehydration/hydration.

The working conditions of TCM systems are determined by the phase diagram of the TCM in question. A phase diagram indicates the conditions under which a certain TCM undergoes hydration or dehydration. In the left bottom corner of Fig. 1, a schematic phase diagram of reaction from Eq. (1) is shown. Applying a condition (combination of water vapor pressure and temperature) below the solid line results in a hydrate  $MX \cdot mH_2O$ . For hydrating this material, a condition should be applied above the solid line. In a system, the temperature of the TCM can be varied with the help of a heat exchanger. Vapor pressure inside the TCM heat storage system is determined by the temperature of the water compartment. Consequently the applied temperature is directly related to the vapor pressure according to the equilibrium line between liquid water and water vapor (the dotted line). The conditions of hydration and dehydration can be found by combining both equilibrium lines in one diagram.

In the case of hydration (producing heat), the initial material in the TCM reactor is  $MX \cdot mH_2O$  and the temperature in the system is  $T_{w1}$ , meaning that the vapor pressure inside the system is equal to  $p_h$ . The applied condition around the TCM in that case is above the equilibrium line between  $MX \cdot mH_2O$  and  $MX \cdot nH_2O$ . Consequently  $MX \cdot mH_2O$  hydrates into  $MX \cdot nH_2O$ . During this reaction the temperature of the TCM reactor will increase as the hydration reaction is an exothermic reaction. As long as the temperature of the TCM reactor is below  $T_h$  the hydration reaction will continue. At temperature  $T_h$ , both phases ( $MX \cdot mH_2O$  and  $MX \cdot nH_2O$ ) can exist as that is the equilibrium temperature corresponding to vapor pressure  $p_h$ . The vapor pressure in the system can only remain constant as the temperature of the water in the system is kept constant. This

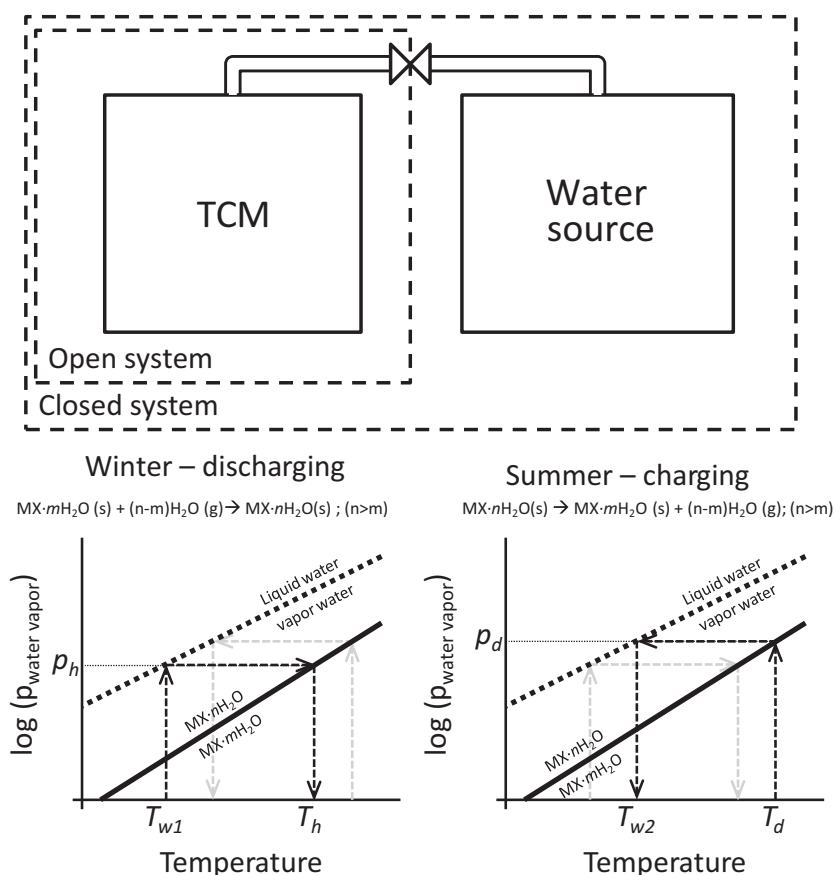


Fig. 1. Top: A schematic overview of a TCM reactor. Bottom: the reactions involved during discharging and charging of the reactor are given.

means in the case of TCM hydration, the evaporation heat of the water should be compensated by heating the water vessel, otherwise the temperature of the water vessel decreases and the vapor pressure in the reactor will decrease. With help of a heat exchanger the reactor can release heat in a controlled way.

Note: we assume that both the temperature of the TCM reactor and water vessel can vary independently from each other.

In the case of dehydration (regenerating the TCM) a certain temperature is applied to the TCM  $T_d$  with a heat exchanger and the reactor is filled with  $MX \cdot mH_2O$ . In that case, the vapor pressure applied to the system by the TCM is equal to  $p_d$ . As long as this vapor pressure is higher than the vapor pressure of the water vessel, the TCM will dehydrate. Since that will cost energy, the TCM should be heated in order to maintain the same vapor pressure. The added water in the gas phase will condensate in the water vessel, which will increase the temperature in the water vessel and the equilibrium vapor pressure in the heat storage system. These losses can be compensated by cooling the water vessel.

In this case, it is assumed that cooling and heating of the water vessel has the same source: a ground pump. In that case the temperature in the vessel  $T_{w2}$  will be higher in the summer than in the winter  $T_{w1}$  as a ground pump delivers a higher temperature in the summer.

### 3. Collection of data

The thermodynamic data on salts are comprised of the following parameters:  $pT$ -data, crystal densities of the considered hydrates, reaction enthalpies, entropies and melting points. A total of 262 salts (563 reactions) were considered (see Table 1), of which the majority of the data originates from The International Critical Tables [36] and Glasser [37]. In case  $pT$  data were not available, they were deduced from the reaction energies [38].

The basic thermodynamic equation for equilibrium between a condensed phase (solid or liquid) and the vapor phase of a pure substance, under conditions of low pressure, is used for this investigation [38]:

$$-\ln \frac{p}{p^0} = \frac{\Delta G_{m \rightarrow n}^0}{RT} = \frac{\Delta H_{m \rightarrow n}^0}{RT} - \frac{\Delta S_{m \rightarrow n}^0}{R}, \quad (2)$$

$$\Delta G_{m \rightarrow n}^0 = \Delta H_{m \rightarrow n}^0 - T \Delta S_{m \rightarrow n}^0,$$

$$\Delta H_{m \rightarrow n}^0 = \left( \sum_{\text{products}} \Delta H_i^0 - \sum_{\text{reactants}} \Delta H_i^0 \right) / (n - m),$$

$$\Delta S_{m \rightarrow n}^0 = \left( \sum_{\text{products}} \Delta S_i^0 - \sum_{\text{reactants}} \Delta S_i^0 \right) / (n - m),$$

wherein  $R$  is the gas constant,  $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ,  $T$  [K] the temperature,  $p$  [bar] the vapor pressure, and  $p^0$  the reference pressure. The enthalpy  $\Delta H_{m \rightarrow n}^0$ , entropy  $\Delta S_{m \rightarrow n}^0$  and Gibbs energy  $\Delta G_{m \rightarrow n}^0$

are all thermodynamic quantities at  $p^0 = 1 \text{ bar}$  and  $T^0 = 298.15 \text{ K}$ . Note that the reaction enthalpy is defined for a certain reaction from an initial ( $m$ ) to a final ( $n$ ) hydration state ( $n > m$ ). For one salt hydrate, different enthalpies of reactions and thus reaction conditions may exist depending on the considered reactions.

The uncertainty of the calculated TCM temperature by a given vapor pressure is calculated with help of a 95% interval. Hereby it is assumed that the error in  $T$ ,  $p^0$  and  $R$  are negligible in Eq. (2). In the error calculations based on enthalpy/entropy data, the error in enthalpy and entropy is taken from the literature source or if the source does not mention the error the maximum error is assumed to be five times the unity of the most significant digit i.e. in case the enthalpy is given by  $40.3 \text{ kJ/mol}$ , the error is assumed to be  $0.5 \text{ kJ/mol}$ .

An example of the error calculation is given in Fig. 2. The  $pT$ -data measured by Polyachenok et al. [39] is plotted, including the calculated data with the help of Eq. (2) and the enthalpy/entropy values of Glasser [38]. Both data sources fit with each other. By small variations in equilibrium vapor pressure observed for  $\text{CuCl}_2$  based on the calculation with Eq. (2), the temperature error of the condenser/evaporator of  $1\text{--}4 \text{ }^\circ\text{C}$  is found in the temperature range of  $0\text{--}100 \text{ }^\circ\text{C}$  to match with a certain hydration/dehydration temperature. In the case the hydration/dehydration temperature is known, the error in pressure is on the order of 10%. This means that the calculated condenser temperature can have an error on the order of  $5 \text{ }^\circ\text{C}$ .

With help of the collected data, various parameters are calculated which are necessary to know for selecting an appropriate hydrate reaction for the foreseen application. The energy density of a system is calculated for an open system (no water storage included in the system) according to the following equation:

$$(E/V)_{\text{open}} = \frac{|\Delta H_{m \rightarrow n}^0| \cdot (n - m)}{M_n} \rho_n, \quad (3)$$

wherein  $M_n$  [kg/mol] is the molar mass of the highest hydrate and  $\rho_n$  [kg/m<sup>3</sup>] the crystal density of the highest hydrate. In case a combined transition of two or more reactions ( $k$ ) is considered, the energy density can be calculated according to:

$$(E/V)_{\text{open}} = \frac{\sum_{i=1}^k |\Delta H_{m_i \rightarrow n_i}^0| \cdot (n_i - m_i)}{M_n} \rho_n. \quad (4)$$

For the closed system (water is stored inside the system), the volume of water molecules involved in the reaction is considered and the energy density is also calculated by:

$$(E/V)_{\text{closed}} = E/V_{\text{open}} \cdot \frac{1}{1 + (n - m) \cdot \frac{\rho_n}{M_n} \cdot \frac{M_w}{\rho_w}}, \quad (5)$$

wherein  $M_w$  [kg/mol] is the molar mass of the liquid water and  $\rho_w$  [kg/m<sup>3</sup>] the density of liquid water. The energy density of both open and closed systems depend strongly on the accuracy of the crystal density and the reaction enthalpy and can be calculated similarly as for the  $T_{\text{TCM}}$ . Although extreme accuracy is taken into account, variations of 2% on the energy densities can be feasible.

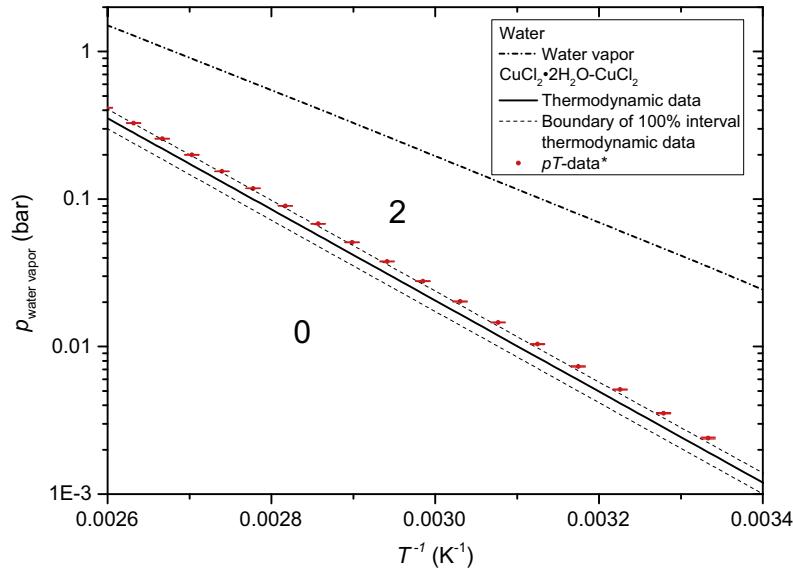
In case the output temperature of the TCM reaction is not sufficient for the targeted heating application, a second heating step is possible. On the basis of the first reaction, water is heated with  $\Delta T$ , generating a vapor pressure necessary for inducing the second reaction wherein the TCM produces the demanded temperature. In that case, the energy density of the system with a double hydration step ( $E/V_{\text{open-II}}$ ) will drop for an open system according to:

$$(E/V)_{\text{open-II}} = (E/V)_{\text{open}} \frac{1}{1 + \left\{ \left( C_p \cdot \Delta T + \frac{|\Delta H_e|}{M_w} \right) (n - m) \rho_n \frac{M_w}{M_n} \right\} / (E/V)_{\text{open}}}, \quad (6)$$

**Table 1**

Overview of the data inside the database.

<b>Considered:</b>	
Salts	262
Reactions	563
<b>Based on:</b>	
$pT$ -data	169
Enthalpy	310
Combined transitions	83
<b>Parameters:</b>	
( $E/V$ )	397
Hydration temperature	563



**Fig. 2.** An example of a phase diagram composed from pT-data from experiments [39] and pT-data calculated with help of thermodynamic data and Eq. (2) [38]. The numbers indicate the water loading in the different regions. Between the water vapor line and the  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} - \text{CuCl}_2$  line, the solid dihydrate will deliquesce, but the exact conditions are unknown.

wherein  $C_p$  [J/(kg·K)] is the heat capacity of liquid water and  $\Delta H_e$  [J/mol] the evaporation enthalpy of water. In a closed system the energy density changes to:

$$(E/V)_{\text{closed-II}} = (E/V)_{\text{open-II}} / \left( 1 + (n-m) \frac{\rho_n}{M_n} \frac{M_w}{\rho_w} \right) \quad (7)$$

The volume variation during hydration/dehydration is calculated on the basis of the crystal structure density according to:

$$\Delta V = \left( 1 - \frac{M_n}{\rho_n} \frac{\rho_m}{M_m} \right) \cdot 100\%. \quad (8)$$

The price is calculated based on price per kg  $P_{kg,i}$ , deducted from the loading  $i$  of the salt hydrate indicated by the supplier and neglecting the cost of water. The price per MJ  $P_{MJ}$  is calculated according to:

$$P_{MJ} = P_{kg,i} \cdot \frac{M_i}{|\Delta H_{m \rightarrow n}^0|} \cdot 10^{-6}. \quad (9)$$

By referring to the current database it is possible to select an appropriate hydrate reaction for any application. As the enthalpy and entropy are known for all reactions in the database, an equilibrium vapor pressure can be found for each TCM temperature and vice versa with the help of Eq. (2). This database will guide the material and system developers during initial screening of suitable hydration/dehydration reactions for particular applications based on crucial demands: output temperature ( $T_{\text{hydration}}$ ), regeneration temperature ( $T_{\text{dehydration}}$ ) and energy density  $E/V$ .

#### 4. Selection procedure

An appropriate TCM for seasonal heat storage should meet a certain set of thermodynamic conditions. These conditions are listed in Table 2. We used two different set of thermodynamic conditions (filters) for selecting suitable candidates. These filters reflect a strict and flexible selection criteria, as explained hereafter. In addition, an analysis is made on non-thermodynamic conditions such as price, chemical stability and safety.

Filter 1 selects a TCM which can fulfill the demands of a particular heat storage system. This heat storage system should be able

**Table 2**

Thermodynamic criteria for selecting hydrates suitable for seasonal heat storage.  $E/V$  in this table refers the energy density of the TCM, whereby only the volume of the TCM is considered. A vapor pressure of 12 and 20 mbar corresponds to respectively a water temperature of 10 and 17 °C.

Filter	1	2
$E/V$ [GJ/m <sup>3</sup> ]	>2	>1.3
<b>Hydration</b>		
$p$ [mbar]	12	12
$T$ [°C]	>65	>50
<b>Dehydration</b>		
$p$ [mbar]	20	20
$T$ [°C]	<100	<120
$T_{\text{melting}}$	> $T_{\text{dehydration}}$	> $T_{\text{dehydration}}$

to store 10 GJ of heat, in order to overcome seasonal fluctuations [35,40], within 10 m<sup>3</sup>. Therefore, an energy density of 2 GJ/m<sup>3</sup> on material level (without considering water storage, open system configuration) is targeted as the reactor system (piping, valves, tubing) and material porosity will decreasing the energy density on system level. Beside volumetric considerations, the TCM should provide temperatures of domestic hot water (DHW) ( $T > 65$  °C) and space heating (HW) ( $T > 40$  °C) within one heating step. This temperature should be reached with a corresponding vapor pressure of 12 mbar, which is equal to an equilibrium vapor pressure of a water source at 10 °C. This 10 °C is based on keeping the temperature of the evaporator constant with help of a borehole based on the ground temperature and the ground temperature at 7 m below surface is approximately 12 °C over the year in the Netherlands [41].

Loading of the heat storage system is foreseen to be performed with heat from solar panels. Different panels are available for domestic applications; flat plate collectors and evacuated tubular collectors. Depending on the specific collector design, different temperatures can be reached, where the power output of the collector depends on the output temperature. In case higher output temperatures are required the total collector energy output in a year will decrease. In this case a dehydration temperature of 100 °C is considered, where a low-cost flat plate reactor can generate 1.8 GJ/m<sup>2</sup> per year [42] with given output temperature. During



dehydration explained as before, the condenser temperature is a significant variable, which will rise during condensation. In order for the dehydration process to continue, the condenser should be cooled. A temperature of 17 °C inside the water drain is considered as reasonable, provided there is a borehole or air cooling. As a consequence, the TCM should dehydrate at a temperature below 100 °C and with a water vapor pressure of 20 mbar. In consideration of mechanical stability, the melting point should be above the dehydration temperature.

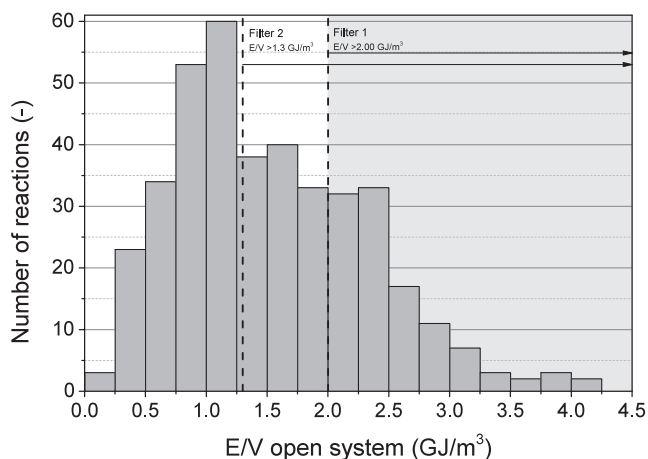
The second filter is introduced as a compromise between the strict boundary conditions for an ideal salt hydrate and achievable boundary conditions acknowledged to available salt hydrates. The energy density is lowered to a value of 1.3 GJ/m<sup>3</sup> on material level, which results in approximately 1 GJ/m<sup>3</sup> in a closed system. The hydration/dehydration temperatures are increased/decreased respectively. This filter will definitely impact system level design, e.g., higher dehydration temperatures and additional heating to reach hot tap water temperatures.

## 5. Database

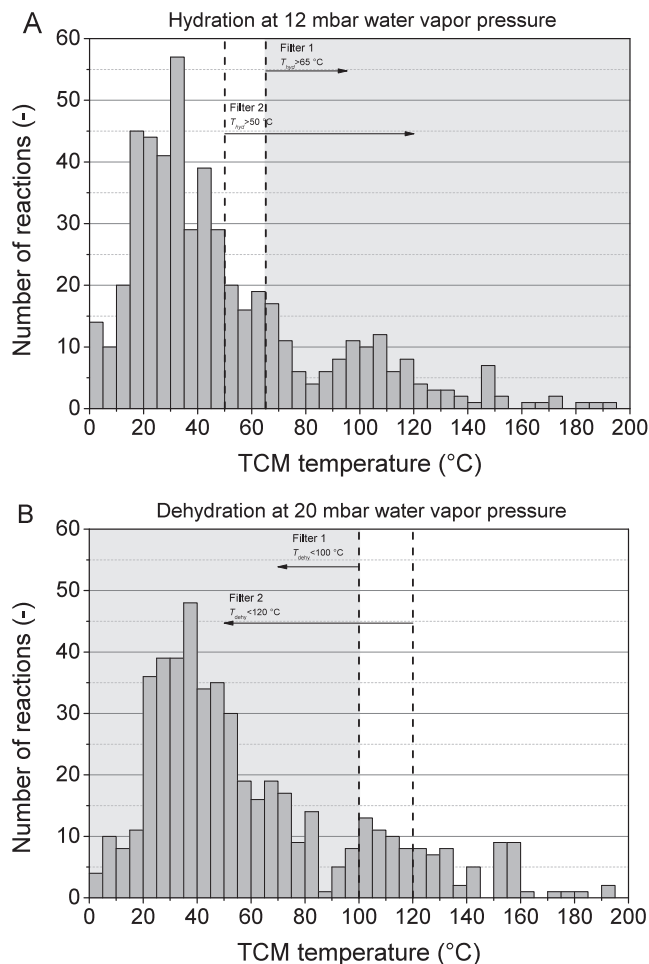
The database consists of 563 entries with complementary thermodynamic data from multiple sources. The full list is given in [Appendix A](#). As mentioned before, different dehydration reactions may occur with one salt. For that reason, multiple hydrate transitions are considered in this database.

A histogram of the energy densities of the available TCM reactions (only 397 records within our database contain information about energy densities) is plotted in [Fig. 3](#). As can be seen, the histogram peaks around 1 GJ/m<sup>3</sup>. The number of hydrate reactions with an energy density above 2 GJ/m<sup>3</sup> (filter 1) is only 114.

Analyzing the maximum hydration and minimum dehydration temperature at the conditions stated in [Table 2](#), two histograms are generated, plotted in [Fig. 4A and B](#), respectively. The shape of the histogram plotting the hydration temperature peaks around 30 °C, implying that most salts have a too low output temperature for generating domestic hot tap water under the applied conditions. Here we stress that hydration reactions of MgSO<sub>4</sub> (monohydrate to hepta- or hexahydrate at 24 and 21 °C, respectively) and CaCl<sub>2</sub> (anhydrous to hexahydrate at 31 °C), often considered as promising salts and extensively investigated [15–19,22,25,26], fail in this respect. Reactions with a TCM temperature below 10 °C are suspicious and indicated as such in [Appendix A](#).



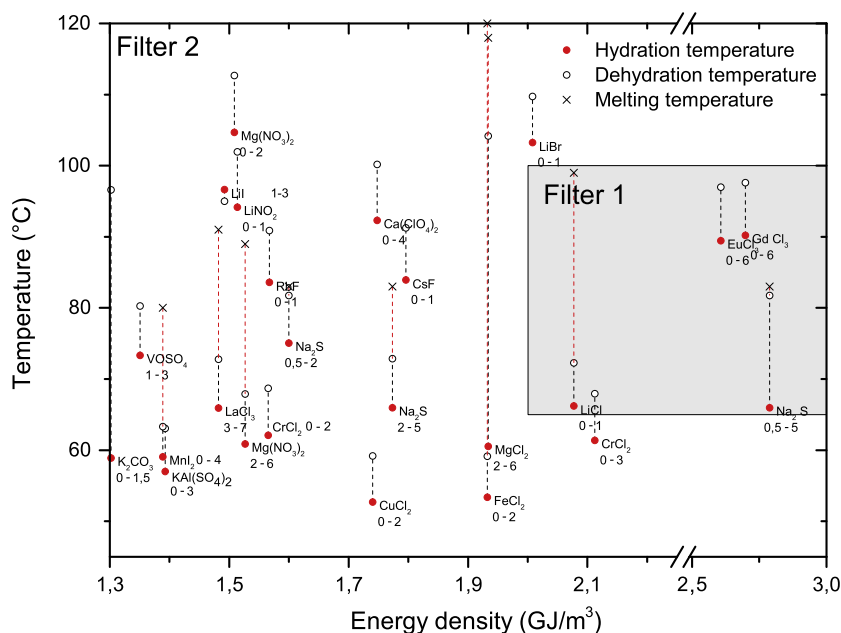
**Fig. 3.** A histogram of the energy density of 361 studied hydration reactions. The reaction energy density is calculated on the basis of the molecular volume of the highest hydrate in the reaction and the enthalpy change.



**Fig. 4.** A histogram of 361 studied hydration reactions showing the maximum hydration temperature with a vapor pressure of 12 mbar (A) and the minimum dehydration temperature with a vapor pressure of 20 mbar (B).

The minimum temperatures necessary for the different dehydration reactions are given in [Fig. 4B](#). This figure shows that most salts lose water readily at 40 °C to a condenser at 20 mbar of water vapor pressure. If the temperature window of filter 1 is applied on this dataset, 165 salts fit the hydration conditions and 415 salts fit the dehydration conditions, respectively. Reactions with a TCM temperature below the 17 °C are suspicious and are indicated as such in [Appendix A](#).

By applying all conditions of filter 1 at once on the dataset, the number of possible TCM candidates reduces to four: Na<sub>2</sub>S, LiCl, EuCl<sub>3</sub> and GdCl<sub>3</sub>. The last two salts are rare earth metals and cannot be used on a large scale with reasonable prices. Furthermore GdCl<sub>3</sub> is toxic (MSDS safety sheet) and LiCl is strongly corrosive [43] and expensive [44], which makes both candidates unfavorable for application. The last material is the most promising of these four materials. It has a high theoretical energy density and the dehydration temperature is relatively low. On the other hand, Na<sub>2</sub>S is corrosive [43,45], reactive [46] with the risk of outgassing of H<sub>2</sub>S [47,48]) and Na<sub>2</sub>S is mentioned as a dual use material by the Australia Group [49]. Beside Na<sub>2</sub>S, the US government considers H<sub>2</sub>S (a potential outgas of Na<sub>2</sub>S) as a high priority chemical threat, as well as being used as a potential weapon of mass destruction by terrorists [48]. Experience with Na<sub>2</sub>S can be found in several heat storage projects like TEPIDIUS [12], SWEAT [24] and MERITS [50,51]. These projects all suffered initially from corrosion and faced variable results by overcoming this issue i.e. by coating all surfaces inside



**Fig. 5.** A selection of the database, which fits the drafted working conditions of filter 1 and/or 2, where the gray shaded area fits the working conditions of filter 1. The maximum hydration and the minimum dehydration temperature of the different hydrate couples are plotted against the reaction energy density on material level (open system). The vapor pressure is equal to 20 mbar and 12 mbar during dehydration and hydration, respectively. In addition the lowest melting temperature of the involved hydrates within the reaction is plotted.

the reactor [51]. Until now, it is unknown how the performance of the coatings will be on time scales of years. Also concerns are raised regarding the release of the last 1.5 water molecules  $\text{Na}_2\text{-S} \cdot 5\text{H}_2\text{O}$ , whereby the melting temperature and dehydration temperature are equal at the current vapor pressure, thereby limiting the loading power [24]. In case no complete dehydration is reached, the energy density will drop from  $2.79 \text{ GJ/m}^3$  to  $1.58 \text{ GJ/m}^3$ . In addition, local variation in the temperature during dehydration can cause melting of the TCM, which challenges the stability of the performance of the heat storage system.

If filter 2 is considered, a shortlist of 25 hydration reactions remains. A summary of thermodynamic conditions is given in Fig. 5. The hydration and dehydration temperatures are plotted against the energy density for the hydration reactions, as well as the known melting temperatures of the hydrates. The initial and final hydration states are indicated below the salt labels. Table 3 gives a more detailed overview of the thermodynamic data and application considerations of these 25 TCM's. In the next section a detailed evaluation of this long list will be performed.

## 6. Evaluation of top 25 reactions

Table 3 lists the hydrate reactions, selected on the basis of filter 2 working conditions. In this section all factors (thermodynamic and non-thermodynamic) are evaluated to arrive at a short-list of TCMs mostly suitable for seasonal heat storage.

### 6.1. Energy density

Heat storage system performance only partly depends on the material energy density. The effective system energy density is dependent on the choice of an open or closed system.

In Fig. 6, the energy density of a pure TCM is plotted against the energy density of a reactor at different porosities. In all cases an open system leads to a higher energy density, but the difference between the open and closed system decreases with increasing porosity. For example, based on Fig. 6, a TCM of  $3.0 \text{ GJ/m}^3$  and a

porosity of 30% in a closed system has a system energy density similar to a TCM material with an energy density of  $1.8 \text{ GJ/m}^3$  and equal porosity in an open system. Practically this means, that in case the  $1 \text{ GJ/m}^3$  at system level is demanded, the material should be at least above  $1.4 \text{ GJ/m}^3$  and  $2.0 \text{ GJ/m}^3$  for an open and closed system, respectively. Hereby, we did not even consider volume for the reactor itself, piping, insulation, valves, control systems, etc.

Besides different energy densities on system level between open and closed system, another important difference exists between these systems. In a closed system, the pressure is minimized (low-pressure/vacuum), and as a result, the vapor transport is extremely fast, however the heat transfer from salt to heat exchanger determines the power output. Conversely, in an open system, the water transport is slow, but the air blown through the system can be used as heat conductive medium. As a result, for both systems, different issues should be considered for a sufficient output power [62].

At this point it is stressed that not all salt hydrates can be used in an open system due to unwanted side effects. For example,  $\text{Na}_2\text{S}$  should be used in a closed system to avoid i.e. the transition of  $\text{Na}_2\text{S}$  into  $\text{Na}_2\text{CO}_3$  as  $\text{Na}_2$  is reactive with  $\text{CO}_2$  from the atmosphere [63]. The best performing reactions solely based on the energy density criterion are  $\text{Na}_2\text{S}$  (0.5–5),  $\text{GdCl}_3$  (0–6) and  $\text{EuCl}_3$  (0–6) in an open as well as a closed system.

### 6.2. Volume variation

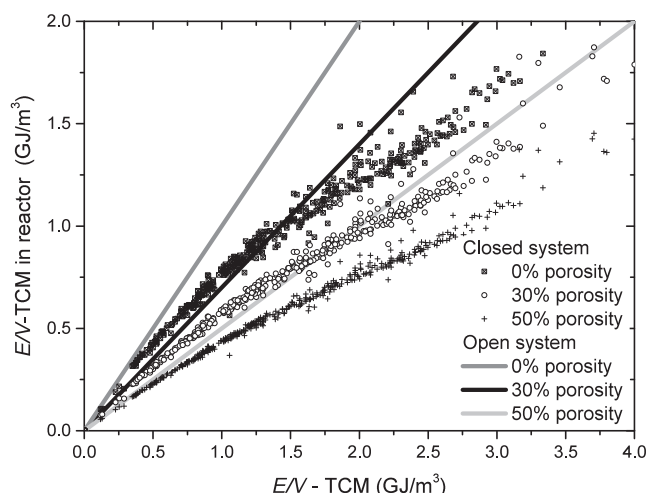
The relative variation of crystal volume during a hydration/dehydration reaction is shown in Table 3. This number is calculated based on the crystal density of highest and lowest hydrates involved in the studied reaction (both listed in Table 3). Fig. 7 shows the crystal volume variation of all considered dehydration reactions in the database against the energy density involved in this reaction. The figure shows a linear trend of 22% volume variation per GJ, meaning that in general the crystal volume varies more in case the energy density of the hydrate increases. Grains are in

**Table 3**

List of the most suitable 25 hydrate reactions based on the working conditions stated in Table 2 with the chosen parameters. The salts are sorted in descending order based on the energy density of an open system. 'Energy densities open system' of salts whereby an open system is unsafe as a result of toxic gas formation are given in *italic* and the energy density of the closed system is used for the ranking. The deliquescence point is based on the vapor pressure whereby the hydrate will form a deliquescence and can no longer transform to a higher hydrate at 25 °C. As a reference, the price is given in euro per kg, which is the price of 1 kg of the stable hydrate under ambient conditions. R: rare earth metal; Tx: acute toxic category 1–3; T: acute toxic category, \*: based on the price of LiCl, \*\*: not exactly known, -: unknown.

Basis	Highest hydrate	Lowest hydrate	Number of hydrates in reaction	Energy density open system (GJ/m <sup>3</sup> )	Energy density closed system (GJ/m <sup>3</sup> )	Density highest hydrate (g/cm <sup>3</sup> ) [52]	Density lowest hydrate (g/cm <sup>3</sup> ) [52]	Volume variation (%)	$T_{hydration}$ (°C) with $p_w = 12$ mbar in reaction	$T_{dehydration}$ (°C) with $p_w = 20$ mbar	Lowest melting point involved (°C)	Deliquescence vapor pressure at 25 °C (mbar)	Price (euro/kg)#	Price (euro/MJ)	LD50 (mg/kg) [53]	Other comments on health	Chemical stability	Based on: $pT$ -data/Enthalpy (H) [source]	Point of concern
GdCl <sub>3</sub>	6	0	2**	2.70	1.56	2.48	4.54	−61	90	98			R		102			H [37]	Rare earth
EuCl <sub>3</sub>	6	0	2**	2.61	1.52	2.42	4.86	−65	89	97			R		3527			H [37]	Rare earth
CrCl <sub>2</sub>	3	0	2	2.11	1.31	2**	3.59	−61**	61	68					1870		Instable Cr <sup>2+</sup>	H [37]	Instable
LiCl	1	0	2	2.08	1.36	1.76	2.09	−41	66	72	99	3.5 [54]	37	35.53	1629			$pT$ [36]	Price
LiBr	1	0	2	2.01	1.37	2.67	3.51	−37	103	110		2 [54]	37*	55	1800			H [37]	Price
FeCl <sub>2</sub>	2	0	2	1.93	1.26	2.39	3.24	−43	53	59	120	10			895		Instable Fe <sup>2+</sup>	H [37]	Instable
CsF	1	0	2	1.79	1.20	4.67	–	–	84	91			>10		N/A			H [37]	Price
Ca(ClO <sub>4</sub> ) <sub>2</sub>	4	0	2	1.75	1.17	2.12	2.8	−33	92	100					4500		Explosive	H [37]	Safety
CuCl <sub>2</sub>	2	0	2	1.74	1.13	2.51	3.39	−42	53	59	>150	21 [55]	3	4.33	584	T		H [37] $pT$ [39]	Price
Na <sub>2</sub> S	5	0.5	3	2.79	1.58	1.58	1.86**	−60**	66	82	82	>11 [56]	0.65	0.51	208		H <sub>2</sub> S formation	$pT$ [56]	Safety/Instable
RbF	1	0	2	1.57	1.10	2.9	3.56	−30	84	91			>10		N/A			H [37]	Price
CrCl <sub>2</sub>	2	0	2	1.57	1.07	2**	3.59	−57	62	69					1870		Instable Cr <sup>2+</sup>	H [37]	Instable
CaCl <sub>2</sub>	2	0	3	1.54	1.06	1.84	2.15	−35	63	111	176	7.8 [57]	0.29	0.52	1940			$pT$ [57]	Deliquescence and higher hydrates
Mg(NO <sub>3</sub> ) <sub>2</sub>	6	2	2	1.53	1.04	1.67	2.03	−41	61	68	89	16			5440		Loss of N <sub>2</sub>	H [37]	Instable
LiNO <sub>2</sub>	1	0	2	1.51	1.07	1.63	–	–	94	102		13 [55]	37*	39	N/A		Loss of N <sub>2</sub>	H [37]	Price
Mg(NO <sub>3</sub> ) <sub>2</sub>	2	0	2	1.51	1.08	2.03	2.36	−31	105	113		16 [54]			5440		Loss of N <sub>2</sub>	H [37]	Instable
LiI	3	1	2	1.49	1.02	2.38	3.18	−40	97	95		5.5 [54]	37*	59	6500			H [37]	Price
LaCl <sub>3</sub>	7	3	2	1.48	1.03	2.23	2.58	−30	66	73	91		R		2370			$pT$ [58]	Rare earth
KAl(SO <sub>4</sub> ) <sub>2</sub>	3	0	2	1.39	1.01	2.2	2.78	−35	57	63	92				6986			$pT$ [36]	Kinetics [59,5]
MnI <sub>2</sub>	4	0	2	1.39	0.90	2.88	5.02	−53	59	63	80				N/A	Tx		H [37]	Safety
VOSO <sub>4</sub>	3	1	2	1.35	0.98	2.28	2.5	−24	73	80			>10		N/A	T		H [37]	Price/Safety
K <sub>2</sub> CO <sub>3</sub>	1.5	0	2	1.30	0.96	2.18	2.33	−22	59	65	>150 °C	14 [54]	1	1.67	1870			H [37] $pT$ [36]	
MgCl <sub>2</sub>	6	2	3	1.93	1.24	1.56	1.89	−47	61	104	117	10 [54]	0.18	0.14	3800		HCl formation	$pT$ [60,61]	Instable
Na <sub>2</sub> S	5	2	2	1.77	1.17	1.58	1.69	−37	66	73	82	>11 [56]	0.65	0.83	208		H <sub>2</sub> S formation	$pT$ [56]	Safety/Instable
Na <sub>2</sub> S	2	0.5	2	1.60	1.14	1.69	1.86**	−38**	75	82	82	>11 [56]	0.65	1.51	208		H <sub>2</sub> S formation	$pT$ [56]	Safety/Instable

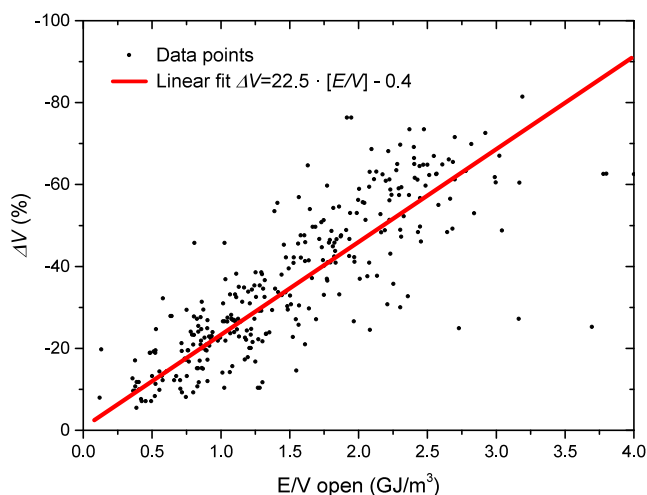




**Fig. 6.** The TCM energy density plotted against the reactor energy density. Different porosities for open and closed systems are considered.

generally dehydrated heterogeneously over the grain and so a grain will not shrink in a regular fashion. As a consequence, void spaces will be formed inside the initial grain as locally pieces of the grain contract. The new formed voids will decrease the mechanical stability of the original grain. This will result in pulverization as the grains are multiple times loaded/unloaded [27]. The pulverization of the grains changes the permeability of the bed and thus the performance of the entire reactor also changes [14]. In addition, swelling and shrinkage of the grains may induce stresses within the heat exchanger.

Another implication of volume changes is related to the heat conductivity of the materials. As for many hydrates the thermal conductivity is on the order of  $0.5 \text{ W m}^{-1} \text{ K}^{-1}$  [64] and that of air is on the order of  $0.024 \text{ W m}^{-1} \text{ K}^{-1}$ , where the empty space in between the grains will act as an insulator. Based on the effective medium theory, the heat conductivity of a grain with 20% or 40% void space within the grain will be reduced by 40% and 70%, respectively [65]. In order to minimize the void space, it is favorable to choose a material with a small volume variation. However, such smaller volume variation is accompanied with a lower energy density (see in Fig. 7).



**Fig. 7.** The volume variation of dehydration reactions plotted against the energy density of the TCM. The linear fit indicates that on average each stored GJ results in a 22% volume variation of the hydrate.

A final note on void spaces within grains should be made regarding reaction kinetics: cracking may open internal pathways in grains for water, which improves water transport and thus heat generation [66]. Thus, a compromise between heat conductivity, water transport and energy density is inevitable.

The reactions in this list with the least volume variations are  $\text{K}_2\text{CO}_3$  (0–1.5),  $\text{VOSO}_4$  (1–3) and  $\text{Mg}(\text{NO}_3)$  (0–2).

### 6.3. Hydration temperature

The hydration temperature indicates the maximum temperature that can be generated in a certain reaction at the given vapor pressure of 12 mbar. This is important in view of the application, as the output temperature of the TCM will determine if a salt is only feasible for domestic heating or also for hot tap water as well. In case the TCM is insufficient for generating the required temperature, additional after-heating is necessary. This can be achieved with electrical heating, but post-heating with a second TCM reactor is an option as well. This can be accomplished by generation of higher vapor pressure at the evaporator.

The temperatures in Table 3 are calculated for a system with a water vapor pressure of 12 mbar. In case the vapor pressure increases, i.e. the evaporator temperature increases, the maximum reaction temperature will increase as well. So, if part of the heat generated with the first reactor is added to the evaporator, a higher reaction temperature can be reached, being of interest to reactions with output temperatures between 50 and 65 °C. The drawback of this approach is the reduction of the effective energy density (see Eqs. (6) and (7)). For example, in case of a 2-step system on  $\text{CuCl}_2$ , wherein the temperature of the evaporator is increased 13 °C to reach an output temperature of 65 °C, the energy density drops from  $1.74 \text{ GJ/m}^3$  to  $1.21 \text{ GJ/m}^3$  and from  $1.13 \text{ GJ/m}^3$  to  $0.72 \text{ GJ/m}^3$  for an open and closed system, respectively. This drop in energy density is significant, but if only part of the volume of TCM is used for domestic hot water, where the drop in energy density of the entire system is less significant.

The reactions with the highest hydration temperatures are  $\text{Mg}(\text{NO}_3)_2$  (0–2),  $\text{LiBr}$  (0–1) and  $\text{LiI}$  (1–3).

### 6.4. Dehydration temperature

The dehydration temperature is the minimum dehydration temperature at which the TCM can dehydrate to the desired loading with a given water vapor pressure of 20 mbar, based on the condenser temperature in the summer. The temperature inside the TCM can be accomplished in several ways e.g., solar collectors, electrical heating, waste heat. The output temperatures of solar collectors strongly depend on the strength of the solar radiation. This radiation intensity fluctuates by strength, depending on the hour of the day, cloudiness and season. Generally a lower dehydration temperature results in a reduction of solar collector surface for the production of the desired temperature and power output [42]. Ideally, the dehydration temperature should be kept as low as possible, to be able to charge the battery multiple times a year. Besides the appropriate salt selection, this also depends on the condenser temperature. In practice, the condenser temperature is the temperature of the water reservoir in summer, i.e. 17 °C in Western European climate.

Based on the dehydration temperature,  $\text{FeCl}_2$  (0–2),  $\text{CuCl}_2$  (0–2),  $\text{KAl}(\text{SO}_4)_2$  (3–12) and  $\text{MnI}_2$  (0–4) are the best reactions, i.e. display the lowest dehydration temperature.

### 6.5. Melting point

During dehydration of pure hydrates, the melting point determines the maximum dehydration temperature. If the temperature

exceeds the melting point, the grains will clog together, which results in a change in porosity of the reactor, affecting the power in- and output. Because of this,  $\text{CaCl}_2$  hexahydrate and tetrahydrate cannot be used as TCM above 40 °C as they have melting points of 30 and 45 °C, respectively. As a consequence the transition of  $\text{CaCl}_2$  (0–2) should be handled with care as during hydration at lower temperatures, the higher hydrates (hexahydrate and tetrahydrate) can be formed. If this is the case, clogging of the grains is still possible in case the grains are heated above the melting points, which makes it challenging to work with  $\text{CaCl}_2$  as a TCM.

As the power during dehydration is strongly affected by the difference in minimum dehydration temperature and applied temperature [67–69], reactions such as  $\text{CuCl}_2$  (0–2),  $\text{K}_2\text{CO}_3$  (0–1.5) and  $\text{FeCl}_2$  (0–2) are more favorable.

### 6.6. Deliquescence vapor pressure

Deliquescence is a key parameter for grain stability both in view of hydration at low temperatures and TCM storage. In case of deliquescence, the grains can clog to each other, changing the local porosity of the TCM. This affects the power which can be delivered/absorbed by the reactor as the vapor transport will be hampered.

The known deliquescence vapor pressures at 25 °C are listed in Table 3, which is only an indication. For specific applications a different temperature should be selected. As can be seen, some hydrates will tend to deliquescence in case the hydration vapor pressure is applied when the TCM is still cold ( $T < 25$  °C). For example  $\text{MgCl}_2$  and  $\text{CaCl}_2$  can deliquescence during the initial hydration process as the TCM is still cold and the vapor pressure of 12 mbar is applied, which is unwanted.

Different strategies for anticipating deliquescence effects can be used. For example a preheating step can avoid deliquescence or start at a lower condenser temperature. Furthermore, deliquescence as well as melting in a TCM reactor might be accepted in case a stabilization technique is used to avoid clogging, such as matrix impregnation [70] or microencapsulation by polymers [71]. A constant grain structure is desired, to secure a steady heating/dehydration rate of the reactor.

Based on the deliquescence criteria,  $\text{CuCl}_2$  (0–2),  $\text{Mg}(\text{NO}_3)_2$  (0–2; 2–6) and  $\text{LiNO}_2$  (0–1) are the most suitable reactions.

### 6.7. Price

The price of the material is a crucial boundary condition affecting the economic feasibility of any heat storage system. For that reason, rare earth metals, like  $\text{EuCl}_3$  and  $\text{GdCl}_3$ , are thus not considered. The prices mentioned in this article are based on industrial scale produced materials where for the real application bulk material will be used as the base material. We tried to estimate the prices of the material as accurately as possible. Hereby, we cooperated with a distributor and manufacturer within the chemical and food market [44] to come up with realistic market prices. The price is given in euro per kg, as a reference, which is the price of 1 kg of the stable hydrate under ambient conditions. The effective price, expressed in euro per joule, determines the actual price per energy.

Based on price as an indicator,  $\text{MgCl}_2$  is currently the most promising candidate, with reservation of bulk price fluctuations for the listed salts in the future. Other good candidates are  $\text{Na}_2\text{S}$  (0.5–5; 2–5) and  $\text{CaCl}_2$  (0–2).

### 6.8. Safety

Safety is an important aspect in the salt selection procedure, as the TCM will be applied in the domestic environment involving all stages of the heat storage system life cycle, from installation, main-

tenance and revision, operation, dismantlement and accidents. Safety impact refers to health effects or environmental damage that may be produced by a chemical.

1. The LD50-values (i.e. Lethal Dosis for 50% of subjects) of the considered salts is listed in Table 3, in which we categorize an LD50 below 25 mg/kg as highly toxic; between 25 and 200 as toxic and between 200 and 2000 as harmful [72]. Based on this classification,  $\text{GdCl}_3$  and  $\text{NiCl}_2$  are toxic, and  $\text{Na}_2\text{S}$  is harmful, but a borderline case. Note that from the point of view of the customer, the LD50 value is merely an indication of health risks, as the customer will not directly interact with the materials.
2. Special attention is devoted to the following hydrates that are explicitly mentioned to be toxic or acute toxic in the MSDS safety sheets:  $\text{MnI}_2$ ,  $\text{VOSO}_4$  and  $\text{CuCl}_2$ , although this is not shown based on the LD50 values.
3. Possible side-reactions due to outgassing or catalytic effect of salts should be addressed case-specifically. Examples are  $\text{H}_2\text{S}$  and  $\text{HCl}$ -formation in the case of  $\text{Na}_2\text{S}$  and  $\text{MgCl}_2$ , respectively.  $\text{Ca}(\text{ClO}_4)_2$  is a strong oxidizing agent, which is of major concern in fires and relevant for working conditions.

### 6.9. Chemical stability of the complexes

A heat battery based on TCMs should reasonably have a service life of about 15–20 years, preferably without replacing the TCM material. A stable material performance is desired, i.e. the TCM should not decompose or transform into another material. Based on this criterion,  $\text{CrCl}_2$  and  $\text{FeCl}_2$  are eliminated from Table 3, since  $\text{Cr}^{2+}$  and  $\text{Fe}^{2+}$  are prone to oxidation in a humid environment [73]. A different oxidation state will affect the  $pT$  characteristics, thus being unwanted.

A second point of concern is the decomposition by outgassing. For example,  $\text{MgCl}_2$  is known to produce  $\text{HCl}$  gas at high temperatures above 140 °C [60], consequently reducing the amount of TCM in the reactor. Recent studies indicate that at dehydration temperatures below 100 °C during cyclic hydration/dehydration  $\text{HCl}$  gas is produced [74]. This reduces the amount of TCM and the  $\text{HCl}$  gas may induce corrosion and increases the pressure inside a closed system.

Although outgassing of  $\text{Na}_2\text{S}$  is not studied as thoroughly as  $\text{MgCl}_2$ , it is mentioned by several scientists that  $\text{Na}_2\text{S}$  can emit  $\text{H}_2\text{S}$  [47,63], which is strongly corrosive. Another hydrate in the list that may decompose under the considered working conditions is  $\text{Mg}(\text{NO}_3)_2$  [75].

For all these hydrates, the stability of the material should be considered in view of the service life duration. The rate of chemical decomposition will determine whether a hydrate should be rejected or not. Current data on decomposition rates are insufficient to exclude the above mentioned hydrates, although these salts are unfavorable as a first choice from this perspective.

### 6.10. Hydration/dehydration kinetics

The reaction kinetics of a TCM have a strong effect on the power in- and output of a heat battery. Generally increasing the  $\Delta T$  between the applied temperature and the minimum dehydration temperature will increase the dehydration rate [76]. This also holds for increasing the vapor pressure: increasing the difference between the applied vapor pressure and the minimum hydration vapor pressure will increase the hydration rate [77].

For most hydrates, multiple dehydration data can be found in literature and in most cases the dehydration data deviate from each other as i.e. the grain size [69], temperature profile [78], sample holder [79] strongly affect the observed characteristics. In general, for each material a single study can be conducted to

summarize all available data whereby the history of the grains is considered. In addition, a similar study can be performed on hydration experiments although the amount of available literature is limited, as controlling the vapor pressure during hydration in a TGA/DSC is complicated.

As we did not perform a study on the hydration/dehydration kinetics for each material, it is difficult to distinguish based on kinetics. One exception we made, based on our own lab experiments and literature [5,59],  $\text{KAl}(\text{SO}_4)_2$  shows very slow (i.e. too slow) hydration reaction kinetics, which we see as problematic for our application.

### 6.11. Short list

The final column of Table 3 summarizes the critical points of concern i.e. potential showstopper for using salt hydrates to store heat under the considered boundary conditions. For the majority of the listed salts, concerns arise regarding the material price, stability of the TCM or safety of the system.  $\text{K}_2\text{CO}_3$  is the only remaining candidate without points of concern, despite the fact it is the lowest-ranked salt in our shortlist in terms of energy density. Note that  $\text{K}_2\text{CO}_3$  can operate in an open system without safety or stability issues, contrary to high potential candidates like  $\text{Na}_2\text{S}$  and  $\text{MgCl}_2$ . The difference in energy density will be strongly reduced in that case. In addition,  $\text{K}_2\text{CO}_3$  performs sufficiently well considering dehydration temperature, melting point, deliquescence point and price. As  $\text{K}_2\text{CO}_3$  is a relatively new salt in view of thermal heat storage, a short overview of the literature is given in Appendix B. Other salts with potential are  $\text{MgCl}_2$ , assuming HCl production can be minimized and deliquescence can be avoided or  $\text{CuCl}_2$  in case of multiple hydration/dehydration cycles a year.

## 7. Conclusion and outlook

An extensive review of 563 hydrate reactions is performed, resulting in a database, wherein the thermodynamic data of these reactions are summarized (see Appendix A). With help of the current database it is possible to select an appropriate hydrate reaction for any application. For example an industry application will have different working temperatures, number of cycles and other safety regulations than applications in households. As the enthalpy and entropy data of 563 hydrate reactions are listed in this database, for each reaction an equilibrium vapor pressure can be found for a given temperature and vice versa. This database will help the material and system developers for performing initial screening on suitable hydration/dehydration reactions for particular applications based on crucial demands: output temperature ( $T_{\text{hydration}}$ ), regeneration temperature ( $T_{\text{dehydration}}$ ) and energy density ( $E/V$ ).

In this study the database is used to evaluate the theoretical potentials and limitations of salt hydrates as thermochemical materials (TCM) for heat storage in the built environment under boundary conditions relevant to (seasonal) use in domestic environments. A list of 25 candidate salts is composed from this database based on four criteria, i.e. energy density on material level above  $1.3 \text{ GJ/m}^3$ , hydration temperature above  $50^\circ\text{C}$ , dehydration temperature below  $120^\circ\text{C}$  and a melting point above the dehydration temperature.

Considering these conditions, commonly suggested salt hydrates like  $\text{CaCl}_2$  (hexa- and tetrahydrate) and  $\text{MgSO}_4$  (hepta- and hexahydrate) did not fit the demands for seasonal heat storage (for domestic heating and hot tap water using the hydration reaction). According to the database, it is impossible to reach the required temperatures during hydration with a reasonable energy storage density.

As the goal of this review is to find a TCM for domestic application over a period of 20–30 years, the list additionally analyzes other critical parameters: safety, chemical stability, kinetics and price. It turns out that almost each material in this top 25 candidate list has its own challenges or foreseen problems. One of the largest problems is the price: eleven selected materials are disregarded after price investigations.

Finally, a single candidate –  $\text{K}_2\text{CO}_3$  – remains from the list of 25 candidate salt hydrates under the boundary conditions considered.  $\text{K}_2\text{CO}_3$  has an energy density on material level that is still 6 times larger than water with a  $\Delta T$  of  $50^\circ\text{C}$  and has no heat loss during storage. By taking into account that the heat storage system also consumes volume, the energy density will drop significantly. Relatively small challenges on system level are expected concerning maintenance, as  $\text{K}_2\text{CO}_3$  is not strongly corrosive, no higher hydrates are known and it has no known unsafe side-reactions. As it does not reveal any decomposition reactions, an open system is an option with  $\text{K}_2\text{CO}_3$ .  $\text{MgCl}_2$  can be considered as a candidate as well provided a solution for HCl-outgassing and deliquescence is found.

The  $1.3 \text{ GJ/m}^3$  energy density of  $\text{K}_2\text{CO}_3$  makes it rarely unlikely that  $10 \text{ GJ}$  of heat will be stored in domestic applications, as this means that the material consumes almost  $8 \text{ m}^3$ , without considering porosity, volume of reactor vessel and heat exchangers. As a consequence, a heat storage system on the basis of  $\text{K}_2\text{CO}_3$  with a single hydration/dehydration cycle a year will be unlikely based on the storage volume. In a multicyclic application, however, the amount of stored heat decreases per cycle, likewise decreasing the amount of material, storage volume and price of the system. Moreover, an increased number of cycles per year appears more feasible when the dehydration temperature is lower. At lower dehydration temperatures, a solar system or waste heat can more easily deliver the required temperature.

A lower dehydration temperature however, means in general a lower hydration (i.e. output) temperature as well. This may be anticipated by increasing the evaporator temperature or by serial application of TCM systems.  $\text{K}_2\text{CO}_3$  has a relatively low dehydration temperature, which may facilitate multiple cycles per year. To further assess its potential as a heat storage material additional TGA/DSC experiments were performed, which will be published subsequently as full papers.

Based on an extensive review of 563 hydrate reactions, no ideal salt exists for seasonal heat storage under the boundary conditions considered. With the current concept of seasonal heat storage, including concepts of closed and open systems, whereby only one dehydration cycle per year is performed and a system energy density of  $1 \text{ GJ/m}^3$ , it is not realistic for large scale implementation to rely on pure salt hydrates as heat storage materials. Although the present view of seasonal heat storage seems unprofitable, multiple usages per year, utilization in peak shaving [80] or storing waste heat [81] are all promising prospects. In conclusion: changing the concepts behind seasonal heat storage is in our view necessary to overcome energy density and price issues, which will provide TCM with an opportunity to be a valid technique for heat storage in the future.

## Acknowledgments

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## Appendix A

Although care is taken to minimize errors in the following table, some mistakes are found during detailed analysis of the table. The data which did not fit lab experiments or seems unrealistic are still included, but indicated with an asterisk \*. As not all materials could be studied in detail, some mistakes will still be unmarked in the table.

Salt gives the basis on the hydrate in the reaction;  $H$  is the highest loading in the reaction;  $L$  the lowest loading in the reaction;  $E/V$  is the energy density of the reaction in an open system without

porosity;  $\Delta H$  is the enthalpy of the reaction;  $\Delta S$  the entropy of the reaction;  $T_{hyd}$  the maximum hydration temperature by 12 mbar water vapor pressure and  $T_{deh}$  the minimum dehydration temperature by 20 mbar water vapor pressure. The used type of thermodynamic data and source is given in column source and in case of the  $pT$  data the minimum and maximum temperature of the used  $pT$  data is given in columns  $T_{min}$  and  $T_{max}$ . For the combined transitions,  $\Delta H$  and  $\Delta S$  are not given, but can be calculated with help of the data of the involved hydrates, which are also given in this table. The error of  $T_{deh}$  is on the order of 1–3 °C, the error in  $E/V$  is on the order of 2%.

Salt	H	L	( $E/V$ ) (GJ/m <sup>3</sup> )	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol·K))	$T_{hy}$ (°C)	$T_{deh}$ (°C)	Source	$T_{min}$ (K)	$T_{max}$ (K)	Comment
AgF	4	2		51.6	139	22	28	H [37]			
AgF	4	1				22	60	Com			
AgF	4	0				22	38	Com			
AgF	2	1		56.2	136	53	60	H [37]			
AgF	2	0				53	38	Com			*
AgF	1	0		59.2	158	33	38	H [37]			
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	6	0	3.19	102.3	150	293	306	H [37]			
Al <sub>2</sub> O <sub>3</sub>	3	1		51.9	156	2	7	H [37]			*
Al <sub>2</sub> O <sub>3</sub>	3	0				2	133	Com			*
Al <sub>2</sub> O <sub>3</sub>	1	0		81.6	169	126	133	H [37]			
Al <sub>4</sub> C <sub>3</sub>	6	0		170.9	141	760	785	H [37]			*
AlCl <sub>3</sub>	6	0	3.78	89.4	154	204	215	H [37]			
AlF <sub>3</sub>	3	0.5	3.00	78.4	152	145	154	H [37]			
As <sub>2</sub> O <sub>5</sub>	4	0		50.3	150	2	6	H [37]			*
AuCl <sub>3</sub>	2	0		56.5	158	20	25	H [37]			
Ba(ClO <sub>4</sub> ) <sub>2</sub>	3	0	3.30	146.6	138	613	634	H [37]			
Ba(IO <sub>3</sub> ) <sub>2</sub>	1	0	0.25	27.0	115	−94	−90	H [37]			*
Ba(N <sub>3</sub> ) <sub>2</sub>	1	0	0.55	44.3	126	1	7	H [37]			*
Ba(OH) <sub>2</sub>	8	7	0.39			43	?	Com			
Ba(OH) <sub>2</sub>	8	3	1.91	58.5	149	43	49	H [37]			
Ba(OH) <sub>2</sub>	8	1.3	2.55			43	?	Com			
Ba(OH) <sub>2</sub>	8	1	2.66			43	39	Com			
Ba(OH) <sub>2</sub>	7	3	1.61			31	49	Com			
Ba(OH) <sub>2</sub>	7	1.3	2.28			31	?	Com			
Ba(OH) <sub>2</sub>	7	1	2.40	58.0	150	31	37	pT [36]	291	338	
Ba(OH) <sub>2</sub>	3	1.3	1.24			33	?	Com			
Ba(OH) <sub>2</sub>	3	1	1.47	57.5	152	33	39	H [37]			
Ba(OH) <sub>2</sub>	1.3	1	0.35	59.0	160	32	38	pT [36]	285	360	
Ba(OH) <sub>2</sub>	1	0	1.08	56.1	127	71	79	pT [36]	350	373	
Ba(OH) <sub>2</sub>	1	0	1.20	60.6	145	61	67	H [37]			
Ba(OH) <sub>2</sub>	0	−1		116.0	92	630	658	pT [36]	903	1263	L:BaO
BaAl <sub>2</sub> O <sub>4</sub>	1	0		83.7	149	183	193	H [37]			
BaBr <sub>2</sub>	2	1	0.58	50.0	135	19	25	pT [36]	293	333	*
BaBr <sub>2</sub>	2	1	0.66	57.3	147	40	46	H [37]			
BaBr <sub>2</sub>	2	1	0.70	61.0	160	38	44	pT [82]	298	378	
BaBr <sub>2</sub>	2	0	1.37			38	42	com			
BaBr <sub>2</sub>	1	0	0.53	40.0	100	21	29	pT [36]	313	348	*
BaBr <sub>2</sub>	1	0	0.76	57.8	151	36	42	H [37]			
BaBr <sub>2</sub>	1	0	0.76	58.0	177	20	23	pT [82]	383	398	
BaCl <sub>2</sub>	6	2		43.5	115	14	21	pT [36]	278	283	
BaCl <sub>2</sub>	6	1				14	39	Com			
BaCl <sub>2</sub>	6	0				14	55	Com			

## Appendix A (continued)

Salt	H	L	(E/V) (GJ/m <sup>3</sup> )	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol·K))	$T_{hy}$ (°C)	$T_{deh}$ (°C)	Source	$T_{min}$ (K)	$T_{max}$ (K)	Comment
BaCl <sub>2</sub>	2	1	0.50	39.3	153	−41	−39	H [37]			*
BaCl <sub>2</sub>	2	1	0.67	53.0	140	32	38	pT [36]	273	323	
BaCl <sub>2</sub>	2	1	0.75	59.0	156	33	39	pT [82]	298	373	
BaCl <sub>2</sub>	2	0	1.50			32	55–109	Com			
BaCl <sub>2</sub>	1	0	0.88	60.0	100	49	55	pT [36]	298	373	*
BaCl <sub>2</sub>	1	0	0.99	67.8	145	101	109	H [37]			
BaCl <sub>2</sub>	1	0	1.17	80.0	190	77	82	pT [82]	373	398	
BaI <sub>2</sub>	6	0	2.21	40.4	100	23	31	pT [36]	293	333	
BaI <sub>2</sub>	2	1	0.55	55.2	147	29	35	H [37]			
BaI <sub>2</sub>	2	0	1.33	66.3	148	29	156	Com			
BaI <sub>2</sub>	1	0	0.86			147	156	H [37]			
BeSO <sub>4</sub>	3	2	0.60	55.7	155	20	26	H [37]			
BeSO <sub>4</sub>	2	1	0.99	70.1	147	109	117	H [37]			
BeSO <sub>4</sub>	2	0	1.97			109	110	Com			
BeSO <sub>4</sub>	1	0	1.27	68.4	146	102	110	H [37]			
Ca(ClO <sub>4</sub> ) <sub>2</sub>	4	0	1.75	64.1	139	92	100	H [37]			
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	1	0		53.2	119	69	78	H [37]			
Ca(IO <sub>3</sub> ) <sub>2</sub>	6	1	1.41	46.4	153	−17	−14	H [37]			*
Ca(IO <sub>3</sub> ) <sub>2</sub>	6	1	1.41	46.4	153	−17	−14	H [37]			*
Ca(IO <sub>3</sub> ) <sub>2</sub>	1	0	0.90	89.9	147	226	237	H [37]			
Ca(NO <sub>3</sub> ) <sub>2</sub>	4	3	0.42	52.5	133	37	44	H [37]			
Ca(NO <sub>3</sub> ) <sub>2</sub>	4	3	0.45	56.0	140	40	47	pT [36]	283	313	
Ca(NO <sub>3</sub> ) <sub>2</sub>	4	3	0.49	61.0	161	34	40	pT [83]	293	315	
Ca(NO <sub>3</sub> ) <sub>2</sub>	4	2	0.86	53.0	135	38	44	pT [83]	293	312	
Ca(NO <sub>3</sub> ) <sub>2</sub>	4	0	1.71	53.0	130	43	50	pT [83]	293	303	
Ca(NO <sub>3</sub> ) <sub>2</sub>	3	2	0.48	55.4	139	43	50	H [37]			
Ca(NO <sub>3</sub> ) <sub>2</sub>	3	2	0.49	55.8	140	43	50	pT [83]	293	324	
Ca(NO <sub>3</sub> ) <sub>2</sub>	3	2	0.52	60.0	140	46	53	pT [36]	288	313	
Ca(NO <sub>3</sub> ) <sub>2</sub>	2	0	1.28	59.5	151	44	51	pT [83]	293	324	
Ca(NO <sub>3</sub> ) <sub>2</sub>	2	0	1.29	60.2	151	48	54	H [37]			
Ca(OH) <sub>2</sub>	0	−1	2.68	88.7	107	349	365	pT [36]	574	830	L:CaO
CaBr <sub>2</sub>	6	0	2.67	61.9	142	74	81	H [37]			
CaCl <sub>2</sub>	6	4 $\alpha$	0.86	54.8	142	35	41	pT [57]	273	301	
CaCl <sub>2</sub>	6	4 $\beta$	0.98	62.6	166	36	42	pT [57]	273	301	
CaCl <sub>2</sub>	6	4	1.03	66.1	182	32	36	H [37]			
CaCl <sub>2</sub>	6	2	2.06			32	49	Com			
CaCl <sub>2</sub>	6	1	2.58			32	71	Com			
CaCl <sub>2</sub>	6	0	3.10			32	71	Com			
CaCl <sub>2</sub>	4 $\alpha$	2	1.21	60.4	155	43	49	pT [57]	273	316	
CaCl <sub>2</sub>	4	2	1.22	60.8	153	48	54	H [37]			
CaCl <sub>2</sub>	4	1	1.82			48	54	Com			
CaCl <sub>2</sub>	4	0	2.46			48	112	Com			
CaCl <sub>2</sub>	2	1	0.63	50.6	114	63	71	pT [57]	273	327	
CaCl <sub>2</sub>	2	1	0.64	51.2	145	63	71	H [37]			
CaCl <sub>2</sub>	2	0	1.54			63	112	Com			
CaCl <sub>2</sub>	1 $\alpha$	0	1.02	59.0	121	103	112	pT [57]	273	365	
CaCl <sub>2</sub>	1 $\beta$	0	1.27	73.0	160	102	109	pT [57]	273	363	
CaCl <sub>2</sub>	1	0	1.28	73.8	140	147	156	H [37]			*
CaC <sub>2</sub> O <sub>4</sub>	1	0	1.06	69.5	134	134	144	H [28]			
CaHPO <sub>4</sub>	2	0	1.66	61.6	150	57	64	H [37]			
CaSeO <sub>4</sub>	2	0		56.8	128	72	80	H [37]			
CaSiF <sub>6</sub>	2	0		75.1	149	133	142	H [37]			
CaSO <sub>3</sub>	2	0.5	1.17	52.4	147	15	20	H [37]			*
CaSO <sub>3</sub>	2	0	1.64			15	68	Com			

(continued on next page)



## Appendix A (continued)

Salt	H	L	(E/V) (GJ/m <sup>3</sup> )	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol·K))	$T_{hy}$ (°C)	$T_{deh}$ (°C)	Source	$T_{min}$ (K)	$T_{max}$ (K)	Comment
CaSO <sub>3</sub>	0.5	0	0.57	62.8	149	65	72	H [37]			
CaSO <sub>4</sub>	2	0.5	1.07	53.6	143	26	32	pT [36]	290	375	
CaSO <sub>4</sub>	2	0.5	1.12	55.4	146	32	37	H [37]			
CaSO <sub>4</sub>	2	0	1.25	46.8	127	14	21	pT [36]			L: soluble
CaSO <sub>4</sub>	2	0	1.29	48.4	129	20	26	pT [36]	288	345	L: natural
CaSO <sub>4</sub>	0.5	0	0.60	65.0	141	94	102	pT [36]	373	435	
CaTeO <sub>3</sub>	1	0	0.70	70.7	147	113	121	H [37]			
Cd(ClO <sub>4</sub> ) <sub>2</sub>	6	4	0.23	20.0	21	66	98	pT [36]	368	598	*
Cd(NO <sub>3</sub> ) <sub>2</sub>	4	2	0.91	57.0	142	47	53	H [37]			
Cd(NO <sub>3</sub> ) <sub>2</sub>	2	0	1.20	57.5	143	48	54	H [37]			
CdBr <sub>2</sub>	4	0	1.82	52.1	145	16	22	H [37]			
CdBr <sub>2</sub>	4	0	1.86	53.3	145	21	27	pT [36]	293	333	
CdCl <sub>2</sub>	2.5	0	1.61	53.4	148	19	24	H [37]			
CdCl <sub>2</sub>	1	0	0.85	53.3	134	40	47	H [37]			
CdSO <sub>4</sub>	2.7	1	1.26	51.5	144	15	20	H [37]			
CdSO <sub>4</sub>	2.7	1	1.30	53.1	147	17	23	pT [36]	298	313	
CdSO <sub>4</sub>	2.7	0	2.25			17	65	Com			
CdSO <sub>4</sub>	1	0	1.08	64.6	158	59	65	H [37]			
CdSO <sub>4</sub>	1	0	3.16	190.0	410	152	155	pT [36]	438	448	
Ce(SO <sub>4</sub> ) <sub>2</sub>	5	0	13.42	384.1	132	2200	2261	H [37]			
CeCl <sub>3</sub>	7	0	2.57	61.0	150	54	60	H [37]			
CePO <sub>4</sub>	2	0	1.57	50.5	151	2	6	H [37]			*
CH <sub>3</sub> NH <sub>2</sub> Al(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.93	65.8	177	36	41	pT [36]	313	349	
CH <sub>3</sub> NH <sub>2</sub> Cr(SO <sub>4</sub> ) <sub>2</sub>	12	0	3.33	74.9	204	39	43	pT [36]	308	352	
CH <sub>3</sub> NH <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	12	0	4.14	93.0	273	27	31	pT [36]	296	315	
Co(ClO <sub>4</sub> ) <sub>2</sub>	6	0	1.06	22.0	27	101	118	pT [36]	360	493	
Co(NO <sub>3</sub> ) <sub>2</sub>	6	0	2.16	56.0	139	46	53	H [37]			
CoBr <sub>2</sub>	6	0	2.61	58.9	149	45	51	H [37]			
CoCl <sub>2</sub>	6	2	1.79	55.5	148	29	35	pT [36]	293	325	
CoCl <sub>2</sub>	6	2	1.84	57.0	153	29	35	H [37]			
CoCl <sub>2</sub>	6	1	2.33			29	50	Com			
CoCl <sub>2</sub>	6	0	2.82			29	105	Com			
CoCl <sub>2</sub>	2	1	0.91	60.3	154	44	50	H [37]			
CoCl <sub>2</sub>	2	0	1.83			44	105	com			
CoCl <sub>2</sub>	1	0	1.03	61.1	129	96	105	H [37]			
CoSO <sub>4</sub>	7	6	0.36	52.6	146	16	22	pT [84]	293	316	
CoSO <sub>4</sub>	7	6	0.37	54.2	150	20	25	H [37]			
CoSO <sub>4</sub>	7	0	2.76			20	47	com			
CoSO <sub>4</sub>	6	1	1.64	42.8	113	13	20	pT [84]	288	339	
CoSO <sub>4</sub>	6	0	2.64	57.5	147	41	47	H [37]			
Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	14	8	1.25	57.7	149	39	45	H [37]			
Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	14	0	4.81			39	292	com			
Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	8	0	3.46	99.6	149	279	292	H [37]			
CrCl <sub>2</sub>	4	3	0.57	58.4	150	41	47	H [37]			
CrCl <sub>2</sub>	4	2	1.18			41	68	com			
CrCl <sub>2</sub>	4	0	2.40			41	69	com			
CrCl <sub>2</sub>	3	2	0.71	62.4	150	61	68	H [37]			
CrCl <sub>2</sub>	3	0	2.11			61	69	com			
CrCl <sub>2</sub>	2	0	1.57	62.2	149	62	69	H [37]			
Cs <sub>2</sub> Co(SO <sub>4</sub> ) <sub>2</sub>	6	2	6.08	348.0	1	26	44	pT [36]	10	302	
Cs <sub>2</sub> CO <sub>3</sub>	3.5	1.5	1.06	64.5	154	65	72	H [37]			
CsAl(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.31	54.8	150	23	28	H [37]			
CsAl(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.78	65.8	170	46	51	pT [36]	323	378	
CsCd(SO <sub>4</sub> ) <sub>2</sub>	6	2	0.48	34.0	90	30	33	pT [36]	299	338	

## Appendix A (continued)

Salt	H	L	( $E/V$ ) (GJ/m <sup>3</sup> )	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol·K))	$T_{hy}$ (°C)	$T_{deh}$ (°C)	Source	$T_{min}$ (K)	$T_{max}$ (K)	Comment
CsCo(SO <sub>4</sub> ) <sub>2</sub>	12	0	3.71	122.5	364	33	36	pT [36]	300	312	
CsCr(SeO <sub>4</sub> ) <sub>2</sub>	12	0	3.08	73.0	196	43	48	pT [36]	323	368	
CsCr(SO <sub>4</sub> ) <sub>2</sub>	12	0	1.67	39.6	103	14	22	pT [36]	287	376	
CsF	1	0	1.80	65.9	148	84	91	H [37]			
CsFe(SO <sub>4</sub> ) <sub>2</sub>	6	4	0.56	64.0	175	31	36	pT [36]	313	363	
CsMg(SO <sub>4</sub> ) <sub>2</sub>	6	2	0.80	45.6	120	19	26	pT [36]	303	341	
CsNi(SO <sub>4</sub> ) <sub>2</sub>	6	2	0.94	53.7	132	45	52	pT [36]	308	355	
CsTi(SO <sub>4</sub> ) <sub>2</sub>	12	0	1.70	56.1	152	24	30	pT [36]	298	368	
CsV(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.01	66.5	178	38	43	pT [36]	323	363	
CsZn(SO <sub>4</sub> ) <sub>2</sub>	6	2	1.11	63.7	166	41	47	pT [36]	308	344	
Cu(ClO <sub>4</sub> ) <sub>2</sub>	8	4	0.29	13.0	−1	111	136	pT [36]	355	472	*
Cu(IO <sub>3</sub> ) <sub>2</sub>	1	0		60.2	154	43	49	H [37]			
Cu(NO <sub>3</sub> ) <sub>2</sub>	6	0		58.0	152	36	41	H [37]			
Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	3	0		46.2	−20	618	649	H [37]			*
CuBr <sub>2</sub>	4	0	2.09	54.8	148	26	31	H [37]			
CuCl <sub>2</sub>	2	0	1.75	58.0	143	50	56	pT [39]	300	415	
CuCl <sub>2</sub>	2	0	1.74	59.1	145	53	59	H [37]			
CuF <sub>2</sub>	2	0	3.04	71.3	152	105	113	H [37]			
CuHPO <sub>4</sub>	1	0	0.63	35.2	−24	563	595	H [37]			*
CuSeO <sub>3</sub>	2	0	1.30	44.1	111	26	34	H [37]			
CuSO <sub>4</sub>	5	3	1.01	55.3	148	28	34	pT [82]	298	369	
CuSO <sub>4</sub>	5	3	1.03	55.9	149	30	35	H [37]			
CuSO <sub>4</sub>	5	1	2.05			30	40	Com			
CuSO <sub>4</sub>	5	0	2.56			30	151	Com			
CuSO <sub>4</sub>	3	1	1.42	56.6	149	34	40	pT [82]	298	390	
CuSO <sub>4</sub>	3	0	2.30			35	151	Com			
CuSO <sub>4</sub>	1	0	0.93	49.4	81	140	151	pT [36]	303	348	
DyCl <sub>3</sub>	6	0	2.87	70.5	143	121	129	H [37]			
DyPO <sub>4</sub>	2	0		107.5	151	322	335	H [37]			
ErCl <sub>3</sub>	6	0	2.94	71.5	147	117	126	H [37]			
ErPO <sub>4</sub>	2	0		99.2	151	271	283	H [37]			
Eu(IO <sub>3</sub> ) <sub>3</sub>	2	0		23.2	−168	2466	2570	H [37]			*
EuCl <sub>3</sub>	6	0	2.61	65.8	145	89	97	H [37]			
EuPO <sub>4</sub>	2	0	1.45	49.0	153	−7	−3	H [37]			*
FeBr <sub>2</sub>	2	1	0.52	50.0	120	71	79	pT [36]	383	403	
FeCl <sub>2</sub>	4	2	1.11	56.1	149	31	36	H [37]			
FeCl <sub>2</sub>	4	0	2.22			31	59	Com			
FeCl <sub>2</sub>	2	1	0.91	62.0	144	73	80	pT [36]	363	398	
FeCl <sub>2</sub>	2	0	1.93	65.8	165	53	59	H [37]			
FeCl <sub>3</sub>	6	0	2.51	62.2	154	53	60	H [37]			
FeI <sub>2</sub>	6	3.5		43.4	101	43	52	pT [36]	363	393	
FePO <sub>4</sub>	6	0	2.17	53.8	150	18	23	H [37]			
FeSO <sub>4</sub>	7	4	1.07	52.0	142	19	25	pT [85]	294	321	
FeSO <sub>4</sub>	7	4	1.10	53.8	147	22	28	H [37]			
FeSO <sub>4</sub>	7	1	2.20			19	26	Com			
FeSO <sub>4</sub>	4	1	1.64	53.4	147	20	26	H [37]			
FeSO <sub>4</sub>	4	0	2.29			20	112	Com			
FeSO <sub>4</sub>	1	0	1.24	71.1	152	104	112	H [37]			
GdCl <sub>3</sub>	6	0	2.70	67.4	149	90	98	H [37]			
GdPO <sub>4</sub>	2	0		111.7	151	348	362	H [37]			
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	2	0	1.38	52.8	131	42	49	pT [36]	248	343	
H <sub>2</sub> O				50.0	141	11	17	H [37]			solid–gas
H <sub>2</sub> SeO <sub>3</sub>	1	0	1.24	53.3	129	49	56	pT [36]	294	384	
H <sub>2</sub> SO <sub>4</sub>	6.5	4		47.0	120	28	35	H [37]			

(continued on next page)

## Appendix A (continued)

Salt	H	L	( $E/V$ ) (GJ/m <sup>3</sup> )	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol·K))	$T_{hy}$ (°C)	$T_{deh}$ (°C)	Source	$T_{min}$ (K)	$T_{max}$ (K)	Comment
H <sub>2</sub> SO <sub>4</sub>	4	3		49.0	120	41	48	H [37]			
H <sub>2</sub> SO <sub>4</sub>	3	2		51.5	120	56	64	H [37]			
H <sub>2</sub> SO <sub>4</sub>	2	1		57.7	124	87	95	H [37]			
H <sub>2</sub> SO <sub>4</sub>	1	0		71.8	134	150	160	H [37]			
H <sub>3</sub> PO <sub>4</sub>	0.5	0		62.8	152	60	66	H [37]			
HIO <sub>3</sub>	1	0	1.97	75.0	201	42	47	pT [36]	293	373	
HoCl <sub>3</sub>	6	0		70.2	148	108	116	H [37]			
HoPO <sub>4</sub>	2	0		109.6	151	335	349	H [37]			
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	2	0	1.21	51.0	124	44	51	pT [36]	323	373	
K <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	0.5	0		53.0	150	21	23	pT [36]	287	313	
K <sub>2</sub> CO(SO <sub>4</sub> ) <sub>2</sub>	6	2		61.0	167	35	39	pT [36]	300	349	
K <sub>2</sub> CO <sub>3</sub>	2	0	1.56	62.5	151	62	69	pT [36]	363	393	dihydrate not observed
K <sub>2</sub> CO <sub>3</sub>	1.5	0.5	0.84	63.6	155	59	65	H [37]			
K <sub>2</sub> CO <sub>3</sub>	1.5	0	1.30			59	65	Com			Direct transition
K <sub>2</sub> CO <sub>3</sub>	0.5	0	0.52	70.2	157	89	97	H [37]			
K <sub>2</sub> CuCl <sub>4</sub>	2	0		59.7	152	44	50	H [37]			
K <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	6	4	0.48	44.0	118	12	19	pT [36]	298	345	
K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub>	6	4	0.44	43.3	116	12	19	pT [36]	300	344	
K <sub>2</sub> Mn(SO <sub>4</sub> ) <sub>2</sub>	6	2	0.83	43.9	117	13	20	pT [36]	328	372	
K <sub>2</sub> Ni(SO <sub>4</sub> ) <sub>2</sub>	6	2	0.95	46.0	112	38	45	pT [36]	307	370	
K <sub>2</sub> SO <sub>3</sub>	1	0		45.6	147	−16	−12	H [37]			*
K <sub>2</sub> Zn(SO <sub>4</sub> ) <sub>2</sub>	6	2	1.12	55.2	146	30	36	pT [36]	289	337	
K <sub>3</sub> PO <sub>4</sub>	7	0		49.9	148	2	7	H [37]			*
K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	3	0	0.69	52.8	142	24	30	pT [36]	288	353	
K <sub>4</sub> Fe(CN) <sub>6</sub>	3	0	0.66	50.2	112	66	74	H [37]			
K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	3	0	1.05	60.7	147	58	64	H [37]			
KAl(SO <sub>4</sub> ) <sub>2</sub>	12	3	1.87	56.0	147	33	39	H [37]			
KAl(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.68	60.3	160	7	8	pT [36]	293	353	*
KAl(SO <sub>4</sub> ) <sub>2</sub>	3	0	1.31	61.8	152	55	61	H [37]			
KAl(SO <sub>4</sub> ) <sub>2</sub>	3	0	1.39	65.9	163	57	63	pT [36]	303	388	
KCr(SO <sub>4</sub> ) <sub>2</sub>	12	6		52.4	141	22	28	pT [36]	283	352	
KF	2	0	2.45	57.0	144	43	49	H [37]			
KOH	2	1	1.10	56.7	147	37	43	H [37]			
KOH	2	0	2.19			37	203	Com			
KOH	1	0.8	0.12	17.9	8	117	141	pT [36]	301	315	
KOH	1	0	2.30	87.1	153	193	203	H [37]			
LaCl <sub>3</sub>	7	3	1.48	61.7	145	66	73	H [38,58]			
LaCl <sub>3</sub>	7	1	2.31			66	114	Com			
LaCl <sub>3</sub>	7	0	2.41			48	158	Com			
LaCl <sub>3</sub>	3	1	1.19	68.9	145	106	114	H [38,58]			
LaCl <sub>3</sub>	3	0	1.81			106	158	Com			
LaCl <sub>3</sub>	1	0	0.83	72.5	136	148	158	H [37]			
LaPO <sub>4</sub>	2	0	3.69	113.8	140	395	411	H [37]			
Li <sub>2</sub> SO <sub>4</sub>	1	0	0.90	55.1	136	48	55	pT [36]	333	381	
Li <sub>2</sub> SO <sub>4</sub>	1	0	0.92	57.2	139	53	60	H [37]			
LiBr	2	1	1.02	56.7	185	−2	1	H [37]			*
LiBr	2	1	1.21	67.5	171	52	57	H [36]			
LiBr	2	0	2.03			52	110	Com			
LiBr	1	0	1.77	69.5	153	94	101	H [37]			
LiBr	1	0	2.01	78.9	173	103	110	H [36]			
LiCl	3	2	0.58	44.6	117	17	24	pT [36]	238	331	
LiCl	3	1	1.41			17	37	Com			
LiCl	3	0	2.22			17	72	Com			
LiCl	2	1	1.22	64.0	173	32	37	pT [36]	273	338	

## Appendix A (continued)

Salt	H	L	( $E/V$ ) (GJ/m <sup>3</sup> )	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol·K))	$T_{hy}$ (°C)	$T_{deh}$ (°C)	Source	$T_{min}$ (K)	$T_{max}$ (K)	Comment
LiCl	2	0	2.43			17	72	Com			
LiCl	1	0	1.83	62.9	145	73	80	H [37]			
LiCl	1	0	2.08	71.3	173	66	72	pT [36]	303	375	
LiClO <sub>4</sub>	3	1	1.44	60.9	146	61	67	H [37]			
LiClO <sub>4</sub>	3	0	2.16			61	59	Com			
LiClO <sub>4</sub>	1	0	1.13	64.0	160	53	59	H [37]			
LiI	3	2	0.75	58.9	123	97	105	H [37]			
LiI	3	2	0.90	71.2	168	75	81	pT [36]	344	385	
LiI	3	1	1.49			75	95	Com			
LiI	3	0	2.24			75	151	Com			
LiI	2	1	0.90	58.9	128	85	93	H [37]			
LiI	2	1	1.09	71.1	161	88	95	pT [36]	350	401	
LiI	2	0	1.80			88	151	Com			
LiI	1	0.5	0.90	86.2	174	136	143	pT [36]	403	451	
LiI	1	0	1.64	78.3	153	142	151	H [37]			
LiNO <sub>2</sub>	1	0	1.51	65.9	143	94	102	H [37]			
LiNO <sub>3</sub>	3	0	2.13	55.6	149	28	34	H [37]			
LiOH	1	0		64.3	161	52	58	H [37]			l:Li <sub>2</sub> O
LiOH	0	−1		106.7	91	563	589	pT [36]	793	1197	l:Li <sub>2</sub> O
LuCl <sub>3</sub>	6	0		65.5	151	76	83	H [37]			
LuPO <sub>4</sub>	2	0		82.4	151	171	180	H [37]			
Mg(ClO <sub>4</sub> )	6	4	0.74	61.7	127	105	114	pT [86]	273	398	
Mg(ClO <sub>4</sub> )	6	2	1.49			105	133	Com			
Mg(ClO <sub>4</sub> )	6	0	2.45			105	225	Com			
Mg(ClO <sub>4</sub> )	4	2	0.80	61.1	118	123	133	pT [86]	273	398	
Mg(ClO <sub>4</sub> )	4	0	1.61			123	225	Com			
Mg(ClO <sub>4</sub> )	2	0	1.33	77.4	124	213	225	pT [86]	273	473	
Mg(NO <sub>3</sub> ) <sub>2</sub>	6	2	1.53	58.6	139	61	68	H [37]			
Mg(NO <sub>3</sub> ) <sub>2</sub>	6	0	2.29			61	113	Com			
Mg(NO <sub>3</sub> ) <sub>2</sub>	2	0	1.51	68.5	145	105	113	H [37]			
Mg(OH) <sub>2</sub> -MgO	0	−1		37.0	87	25	35	pT [36]	308	444	l:MgO
MgBr <sub>2</sub>	6	1	1.74	50.0	135	19	25	pT [36]	293	333	
MgBr <sub>2</sub>	6	0	3.02	72.5	142	135	144	H [37]			
MgBr <sub>2</sub>	1	0	1.19	69.0	145	109	116	pT [36]	393	438	
MgCl <sub>2</sub>	6	4	0.80	52.0	118	65	72	pT [61]	293	367	
MgCl <sub>2</sub>	6	4	0.85	55.5	130	61	68	pT [87]	305	403	
MgCl <sub>2</sub>	6	4	0.89	58.2	138	61	68	H [37]			
MgCl <sub>2</sub>	6	2	1.93			61	104	Com			
MgCl <sub>2</sub>	6	1	2.48			61	127	Com			
MgCl <sub>2</sub>	6	0	3.12			61	214	Com			
MgCl <sub>2</sub>	4	2	1.25	64.6	140	93	101	pT [61]	293	405	
MgCl <sub>2</sub>	4	2	1.32	67.8	147	96	104	H [37]			
MgCl <sub>2</sub>	4	1	2.01			96	127	Com			
MgCl <sub>2</sub>	4	0	2.82			96	214	Com			
MgCl <sub>2</sub>	2	1	1.01	70.3	143	117	125	H [60]			
MgCl <sub>2</sub>	2	1	1.03	71.3	146	118	127	H [37]			
MgCl <sub>2</sub>	2	0	2.23			118	214	Com			
MgCl <sub>2</sub>	1	0		83.5	141	203	214	H [37]			
MgCO <sub>3</sub>	5	3		53.0	146	20	25	H [37]			
MgCO <sub>3</sub>	3	1		51.9	145	15	21	H [37]			
MgSeO <sub>3</sub>	6	0		58.4	152	38	43	H [37]			
MgSeO <sub>4</sub>	6	4	0.74	52.7	147	17	22	H [37]			
MgSeO <sub>4</sub>	4	1		56.4	147	35	41	H [37]			
MgSeO <sub>4</sub>	1	0	1.52	88.4	84	421	440	H [37]			

(continued on next page)

## Appendix A (continued)

Salt	H	L	( $E/V$ ) (GJ/m <sup>3</sup> )	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol·K))	$T_{hy}$ (°C)	$T_{deh}$ (°C)	Source	$T_{min}$ (K)	$T_{max}$ (K)	Comment
MgSO <sub>3</sub>	6	3		55.9	142	41	47	H [37]			
MgSO <sub>3</sub>	3	0		64.1	150	70	77	H [37]			
MgSO <sub>4</sub>	7	6	0.40	59.6	166	24	29	H [38,88]			
MgSO <sub>4</sub>	7	4	1.13	55.6	145	24	29	H [38,88]			
MgSO <sub>4</sub>	7	1	2.27	56.0	141	24	28	H [38,88]			
MgSO <sub>4</sub>	6	5	0.37	49.7	144	6	11	H [38,88]			*
MgSO <sub>4</sub>	6	4	0.80	53.4	138	24	30	H [38,88]			
MgSO <sub>4</sub>	6	1	2.08	55.2	137	22	28	H [38,88]			
MgSO <sub>4</sub>	5	4		57.8	145	46	52	H [38,88]			
MgSO <sub>4</sub>	4	2	1.23	58.8	143	55	61	H [37]			
MgSO <sub>4</sub>	2	1		41.6	148	−33	−29	H [37]			*
MgSO <sub>4</sub>	1	0	2.00	107.9	154	315	329	H [37]			
MgTeO <sub>3</sub>	6	5		52.7	147	17	22	H [37]			
MgTeO <sub>3</sub>	5	0		61.0	147	59	66	H [37]			
Mn(ClO <sub>4</sub> ) <sub>2</sub>	6	4		20.0	18	103	127	pT [36]	373	470	
MnBr <sub>2</sub>	6	4		76.5	139	166	176	H [37]			*
MnBr <sub>2</sub>	4	1	1.16	41.7	101	32	40	pT [36]	293	373	
MnBr <sub>2</sub>	4	0	2.22	59.7	150	47	53	H [89]			
MnBr <sub>2</sub>	1	0		76.0	163	111	117	pT [36]	413	433	
MnCl <sub>2</sub>	4	2	1.05	51.0	134	27	33	pT [36]	293	353	
MnCl <sub>2</sub>	4	2	1.14	55.7	147	32	37	H [37]			
MnCl <sub>2</sub>	4	1	1.79			32	74	Com			
MnCl <sub>2</sub>	4	0	2.45			32	122	Com			
MnCl <sub>2</sub>	2	1	0.89	63.6	150	68	74	H [37]			
MnCl <sub>2</sub>	2	0	1.78			68	122	Com			
MnCl <sub>2</sub>	1	0	1.10	63.5	128	114	122	H [37]			
MnF <sub>2</sub>	4			50.2	147	5	10	H [37]			*
MnI <sub>2</sub>	4	2	0.83	55.2	130	59	67	pT [36]	323	383	
MnI <sub>2</sub>	4	1	1.11			59	63	Com			
MnI <sub>2</sub>	4	0	1.39			59	63	Com			
MnI <sub>2</sub>	2	1	0.38	37.0	77	52	63	pT [36]	339	393	*
MnI <sub>2</sub>	1	0	0.53	43.1	95	53	63	pT [36]	393	406	
MnSeO <sub>4</sub>	1	0		78.2	82	357	374	H [37]			
MnSO <sub>4</sub>	7	5	0.74	51.0	149	6	11	H [37]			*
MnSO <sub>4</sub>	4	1	1.58	52.0	150	10	14	H [37]			*
MnSO <sub>4</sub>	2	1		46.3	124	16	22	pT [36]	282	333	
MnSO <sub>4</sub>	1	0	0.79	45.1	108	40	48	pT [36]	293	333	
MnSO <sub>4</sub>	1	0	1.22	69.5	146	108	116	H [37]			
MoO <sub>3</sub>	1	0		85.6	107	319	334	H [37]			
Na <sub>0.96</sub> Al <sub>0.96</sub> Si <sub>2.04</sub> O <sub>6</sub>	0.5	0		84.5	134	229	240	H [37]			
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	10	0		55.5	149	28	33	H [37]			
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	5	0		72.8	192	46	51	pT [36]	333	338	
Na <sub>2</sub> C <sub>2</sub> H <sub>4</sub> O <sub>6</sub>	2	0		44.5	119	13	20	pT [36]	282	322	
Na <sub>2</sub> CO <sub>3</sub>	10	7	0.78	51.0	140	16	22	pT [36]	248	305	
Na <sub>2</sub> CO <sub>3</sub>	10	7	0.84	54.6	141	35	42	H [37]			
Na <sub>2</sub> CO <sub>3</sub>	7	1	2.08	51.6	146	13	18	H [37]			
Na <sub>2</sub> CO <sub>3</sub>	1	0	1.07	58.6	155	33	39	pT [36]	293	371	
Na <sub>2</sub> CO <sub>3</sub>	1	0	1.08	59.4	156	36	42	H [37]			
Na <sub>2</sub> CrO <sub>4</sub>	4	0		54.5	143	32	38	H [37]			
Na <sub>2</sub> HAsO <sub>4</sub>				46.4	120	24	30	pT [36]	273	373	
Na <sub>2</sub> HPO <sub>4</sub>	12	7	0.86	40.0	99	22	28	pT [36]	248	323	
Na <sub>2</sub> HPO <sub>4</sub>	12	7	1.15	53.7	149	19	24	H [37]			
Na <sub>2</sub> HPO <sub>4</sub>	7	2	1.56	49.8	132	22	28	pT [36]	273	372	
Na <sub>2</sub> HPO <sub>4</sub>	7	2	1.66	53.2	146	21	26	H [37]			



## Appendix A (continued)

Salt	H	L	(E/V) (GJ/m <sup>3</sup> )	ΔH (kJ/mol)	ΔS (J/(mol·K))	T <sub>hy</sub> (°C)	T <sub>deh</sub> (°C)	Source	T <sub>min</sub> (K)	T <sub>max</sub> (K)	Comment
Na <sub>2</sub> HPO <sub>4</sub>	2	0		57.2	156	26	31	H [37]			
Na <sub>2</sub> S	9	5	1.32	55.3	148	27	33	pT [56]	278	317	
Na <sub>2</sub> S	5	2	1.77	62.9	149	66	73	pT [56]	288	356	
Na <sub>2</sub> S	5	0.5	2.79			66	82	Com			
Na <sub>2</sub> S	2	0.5	1.60	72.0	171	75	82	pT [56]	278	353	
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	5	0	1.91	54.0	145	26	32	H [37]			
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	5	0	1.95	54.9	144	32	38	pT [36]	288	313	
Na <sub>2</sub> SiO <sub>3</sub>	9	8		53.1	174	−7	−4	H [37]			*
Na <sub>2</sub> SiO <sub>3</sub>	8	6		53.8	147	22	28	H [37]			
Na <sub>2</sub> SiO <sub>3</sub>	6	5		51.9	139	24	30	H [37]			
Na <sub>2</sub> SiO <sub>3</sub>	5	0		52.6	135	34	41	H [37]			
Na <sub>2</sub> SO <sub>3</sub>	7	0		52.1	145	16	22	H [37]			
Na <sub>2</sub> SO <sub>4</sub>	10	7	0.77	52.1	145	16	22	H [37]			
Na <sub>2</sub> SO <sub>4</sub>	10	0	2.48	50.5	139	15	21	pT [90]	273	306	
Na <sub>2</sub> SO <sub>4</sub>	7	0	2.21	53.7	151	16	21	H [37]			
Na <sub>2</sub> WO <sub>4</sub>	2	0		55.3	148	28	34	H [37]			
Na <sub>3</sub> PO <sub>4</sub>	12	0		55.1	148	27	33	H [37]			
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	10	0		54.1	147	24	29	H [37]			
NaAl(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.40	54.9	151	21	27	pT [36]	304	332	
NaAl(SO <sub>4</sub> ) <sub>2</sub>	12		2.32	53.1				H [37]			
NaAl(SO <sub>4</sub> ) <sub>2</sub>	12		2.44	55.9				H [37]			
NaBr	2	0	1.67	53.1	145	21	27	H [37]			
NaBr	2	0	1.69	53.7	143	27	33	pT [91]	283	324	
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	3	1.5	0.94	58.7	157	30	36	pT [36]	288	323	
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	3	0				30	36	Com			
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	1.5	0	1.22	58.0	152	34	40	pT [36]	288	308	
NaClO <sub>2</sub>	3	0	2.00	55.9	149	30	35	H [37]			
NaClO <sub>4</sub>	1	0	0.71	47.8	147	−6	−2	H [37]			*
NaCN	2	0.5	1.30	54.1	148	22	28	H [37]			
NaCN	2	0	1.75			22	33	Com			
NaCN	0.5	0	0.71	55.2	148	28	33	H [37]			
NaCr(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.30	55.2	146	32	37	pT [36]	324	363	
NaHC <sub>2</sub> O <sub>4</sub>	3	0		51.8	134	30	37	pT [36]	248	323	
NaHSO <sub>4</sub>	1	0		52.3	134	34	41	H [37]			
NaI	2	0	1.47	55.2	139	42	49	pT [36]	295	333	
NaI	2	0	1.53	57.3	151	34	39	H [37]			
NaIO <sub>3</sub>	5	1	1.78	51.4	149	8	13	H [37]			*
NaIO <sub>3</sub>	5	0	2.23			8	105	com			*
NaIO <sub>3</sub>	1	0	1.10	68.4	148	98	105	H [37]			
NaKC <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	4	0		56.7	153	26	31	pT [36]	288	313	
NaOH	1	0	1.46	50.0	100	93	102	pT [36]	273	323	h: unclear
NaOH	1	0	1.97	65.3	169	45	50	H [37]			*
Nd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2	0		83.2	141	201	212	H [37]			
NdCl <sub>3</sub>	6	0		61.7	150	58	64	H [37]			
NdPO <sub>4</sub>	2	0		111.7	136	395	411	H [37]			
(NH <sub>2</sub> OH) Al(SO <sub>4</sub> ) <sub>2</sub>	12	0		70.0	180	31	36	pT [36]	300	348	
(NH <sub>2</sub> OH) Cr(SO <sub>4</sub> ) <sub>2</sub>	12	0		70.0	180	31	36	pT [36]	303	345	
(NH <sub>4</sub> ) <sub>2</sub> Co(SO <sub>4</sub> ) <sub>2</sub>	6	2	0.94	62.0	160	41	47	pT [36]	308	355	
(NH <sub>4</sub> ) <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub>	6	4		58.0	152	34	40	pT [36]	302	341	
(NH <sub>4</sub> ) <sub>2</sub> Mn(SO <sub>4</sub> ) <sub>2</sub>	6	2		47.0	120	19	25	pT [36]	339	363	
(NH <sub>4</sub> ) <sub>2</sub> Zn(SO <sub>4</sub> ) <sub>2</sub>	6	2	1.22	64.0	170	46	52	pT [36]	304	353	
(NH <sub>4</sub> ) V(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.59	59.0	160	33	39	pT [36]	323	363	
NH <sub>4</sub> (UO <sub>2</sub> ) <sub>2</sub> F <sub>5</sub>	4	3		48.5	131	18	24	H [37]			
NH <sub>4</sub> (UO <sub>2</sub> ) <sub>2</sub> F <sub>5</sub>	4	0		48.5	131	18	55	H [37]			

(continued on next page)

## Appendix A (continued)

Salt	H	L	( $E/V$ ) (GJ/m <sup>3</sup> )	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol·K))	$T_{hy}$ (°C)	$T_{deh}$ (°C)	Source	$T_{min}$ (K)	$T_{max}$ (K)	Comment
NH <sub>4</sub> (UO <sub>2</sub> ) <sub>2</sub> F <sub>5</sub>	3	0		17.2	20	31	55	H [37]			
NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub>	3	1		65.7	174	41	46	pT [36]	323	362	
NH <sub>4</sub> Co(SO <sub>4</sub> ) <sub>2</sub>	12	0	4.15	95.6	293	18	21	pT [36]	288	309	
NH <sub>4</sub> Cr(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.44	56.3	150	30	36	pT [36]	323	359	
NH <sub>4</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	12	0	4.00	90.0	260	28	32	pT [36]	298	314	
Ni(ClO <sub>4</sub> ) <sub>2</sub>				17.9	15	106	132	pT [36]	357	541	
Ni(IO <sub>3</sub> ) <sub>2</sub>	2	0	0.75	41.6	168	−33	−31	H [37]			*
Ni(NO <sub>3</sub> ) <sub>2</sub>	6			58.2	136	64	72	H [37]			
NiCl <sub>2</sub>	6	4	0.72	46.0	119	23	30	pT [36]	288	308	
NiCl <sub>2</sub>	6	4	0.80	51.3	138	22	28	H [37]			
NiCl <sub>2</sub>	6	2	1.73			22	37	Com			
NiCl <sub>2</sub>	6	0	2.70			22	76	Com			
NiCl <sub>2</sub>	4	2	0.81	47.0	119	30	37	pT [36]	288	339	
NiCl <sub>2</sub>	4	2	1.03	59.8	160	33	38	H [37]			
NiCl <sub>2</sub>	4	0	2.09			33	76	Com			
NiCl <sub>2</sub>	2	0	1.97	62.2	145	69	76	H [37]			
NiSO <sub>4</sub>	7	6	0.36	51.7	144	16	21	H [37]			
NiSO <sub>4</sub>	7	4				16	?	Com			
NiSO <sub>4</sub>	7	1				16	45	Com			
NiSO <sub>4</sub>	7	0				16	571	Com			
NiSO <sub>4</sub>	4	1	1.82	57.7	149	39	45	H [37]			
NiSO <sub>4</sub>	4	0	2.31	54.8	143	39	571	H [37]			
NiSO <sub>4</sub>	1	0	0.90	46.3	125	14	20	pT [36]	288	348	*
NiSO <sub>4</sub>	1	0	2.73	140.3	144	551	571	H [37]			
Pb(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub>	3	0		16.0	−7	170	195	pT [36]	288	295	*
PrCl <sub>3</sub>	7	6		64.4	150	72	79	H [37]			
PrCl <sub>3</sub>	6	0		61.6	151	55	62	H [37]			
PtCl <sub>4</sub>	5	0		62.9	163	43	48	H [37]			
PuCl <sub>3</sub>	6	0		60.5	146	58	65	H [37]			
PuO <sub>2</sub> (OH) <sub>2</sub>	1	0		34.1	103	−31	−24	H [37]			*
Ra(BrO <sub>3</sub> ) <sub>2</sub>	1	0		60.2	143	62	69	H [37]			
Ra(IO <sub>3</sub> ) <sub>2</sub>	1	0		51.2	154	2	6	H [37]			*
RaBr <sub>2</sub>	2	0		59.7	154	41	47	H [37]			
RaCl <sub>2</sub>	2	0		57.7	151	36	41	H [37]			
RaI <sub>2</sub>	0.5	0		70.2	143	119	127	H [37]			
Rb <sub>2</sub> Cd(SO <sub>4</sub> ) <sub>2</sub>	6	2		44.6	119	14	20	pT [36]	301	341	
Rb <sub>2</sub> Co(SO <sub>4</sub> ) <sub>2</sub>	6	2	1.16	60.0	156	38	44	pT [36]	301	349	
Rb <sub>2</sub> CO <sub>3</sub>	3.5	1.5	0.87	51.3	153	3	8	H [37]			*
Rb <sub>2</sub> CO <sub>3</sub>	3.5	1	1.17			3	105	Com			*
Rb <sub>2</sub> CO <sub>3</sub>	3.5	0	1.73			3	81	Com			*
Rb <sub>2</sub> CO <sub>3</sub>	1.5	1	0.42	69.5	151	98	105	H [37]			
Rb <sub>2</sub> CO <sub>3</sub>	1.5	0	1.23			98	81	Com			
Rb <sub>2</sub> CO <sub>3</sub>	1	0	0.87	66.5	155	74	81	H [37]			
Rb <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub>	6	4	0.51	53.1	141	27	33	pT [36]	302	340	
Rb <sub>2</sub> Mn(SO <sub>4</sub> ) <sub>2</sub>	6	2		47.2	127	17	23	pT [36]	301	368	
Rb <sub>2</sub> Ni(SO <sub>4</sub> ) <sub>2</sub>	6	2		49.1	117	48	56	pT [36]	306	388	
Rb <sub>2</sub> Zn(SO <sub>4</sub> ) <sub>2</sub>	6	2	1.27	65.3	170	44	49	pT [36]	306	355	
RbAl(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.47	57.0	148	37	43	pT [36]	323	370	
RbAl(SO <sub>4</sub> ) <sub>2</sub>	12	0	2.50	57.7	149	39	45	H [37]			
RbCr(SO <sub>4</sub> ) <sub>2</sub>	12	0		56.0	150	29	35	pT [36]	313	363	
RbF	1	0	1.57	66.2	149	84	91	H [37]			
RbFe(SO <sub>4</sub> ) <sub>2</sub>	12	0	3.80	87.0	250	31	35	pT [36]	298	329	
RbOH	2	1	1.12	62.8	147	69	76	H [37]			
RbOH	2	0				69	211	Com			

## Appendix A (continued)

Salt	H	L	( $E/V$ ) (GJ/m <sup>3</sup> )	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol·K))	$T_{hy}$ (°C)	$T_{deh}$ (°C)	Source	$T_{min}$ (K)	$T_{max}$ (K)	Comment
RbOH	1	0	2.08	88.3	153	200	211	H [37]			
RbTi(SO <sub>4</sub> ) <sub>2</sub>	12	0		68.3	180	43	48	pT [36]	313	378	
RbV(SO <sub>4</sub> ) <sub>2</sub>	12	0		57.1	153	30	35	pT [36]	326	364	
ScCl <sub>3</sub>				71.2	149	111	119	H [37]			
SmCl <sub>3</sub>	6	0		65.6	150	78	85	H [37]			
SmPO <sub>4</sub>	2	0		115.9	145	393	408	H [37]			
Sr(BrO <sub>3</sub> ) <sub>2</sub>	1	0		138.9	147	532	551	H [37]			
Sr(IO <sub>3</sub> ) <sub>2</sub>	6	1	1.97	53.6	156	10	14	H [37]			
Sr(IO <sub>3</sub> ) <sub>2</sub>	6	0	2.36			10	45	Coms			
Sr(IO <sub>3</sub> ) <sub>2</sub>	1	0	0.52	52.0	131	38	45	H [37]			
Sr(NO <sub>3</sub> ) <sub>2</sub>	4	0		51.3	145	12	18	H [37]			
Sr(OH) <sub>2</sub>	8	2	1.63	38.0	101	18	24	pT [36]	288	363	
Sr(OH) <sub>2</sub>	2	1	0.84	41.7	100	35	43	pT [36]	327	373	
Sr(OH) <sub>2</sub>	0	−1	2.39	98.0	97	570	575	pT [36]	703	1051	L: SrO
SrBr <sub>2</sub>	6	1	1.94	56.5	141	45	52	pT [82]	298	360	
SrBr <sub>2</sub>	6	1	1.99	57.9	144	48	54	H [7,38]			
SrBr <sub>2</sub>	6	0	1.77	43.0	96	52	61	pT [36]	293	313	*
SrBr <sub>2</sub>	6	0	2.49			48	122	Com			
SrBr <sub>2</sub>	1	0	1.06	72.8	152	114	122	H [37]			
SrCl <sub>2</sub>	6	2	1.58	53.7	143	27	33	pT [82]	298	333	
SrCl <sub>2</sub>	6	2	1.61	54.6	146	28	33	H [37]			
SrCl <sub>2</sub>	6	2	1.87	63.7	175	28	34	pT [36]	248	323	
SrCl <sub>2</sub>	6	1	2.04			28	52	Com			
SrCl <sub>2</sub>	6	0	2.99			28	202	Com			
SrCl <sub>2</sub>	2	1	0.83	58.9	148	46	52	pT [82]	298	403	
SrCl <sub>2</sub>	2	1	0.83	59.4	91	189	202	H [37]			
SrCl <sub>2</sub>	2	0	1.54	55.0	138	45	52	pT [36]	293	373	
SrCl <sub>2</sub>	1	0	1.01	61.1	184	12	15	H [37]			*
SrTeO <sub>3</sub>	1	0		64.0	147	75	83	H [37]			
TbCl <sub>3</sub>	6	0		70.2	148	108	116	H [37]			
TbPO <sub>4</sub>	2	0		103.4	151	297	310	H [37]			
Tc <sub>2</sub> O <sub>7</sub>	1	0		45.8	102	58	67	H [37]			
Th(NO <sub>3</sub> ) <sub>4</sub>	5	4		47.3	148	−10	−5	H [37]			*
Th(NO <sub>3</sub> ) <sub>4</sub>	5	0				−10	155	Com			*
Th(NO <sub>3</sub> ) <sub>4</sub>	4	0		76.4	147	146	155	H [37]			
ThF <sub>4</sub>	2.5	0		60.6	154	45	51	H [37]			
Tl(Al(SO <sub>4</sub> )) <sub>2</sub>	12	0		68.9	184	41	46	pT [36]	324	362	
Tl(Cr(SO <sub>4</sub> )) <sub>2</sub>	12	0		58.6	157	31	36	pT [36]	306	375	
TlOH	0.5	0		52.4	126	53	60	pT [36]	319	413	
TmPO <sub>4</sub>	2	0		103.4	151	297	310	H [37]			
U(SO <sub>4</sub> ) <sub>2</sub>	8	4		53.0	144	22	28	H [37]			
U(SO <sub>4</sub> ) <sub>2</sub>	4	0		51.6	144	15	21	H [37]			
UF <sub>4</sub>	2.5	0		61.1	144	65	72	H [37]			
(UO <sub>2</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>				52.8		15	20	H [37]			
(UO <sub>2</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>				70.1		116	124	H [37]			
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	6	3		53.9	143	28	34	H [37]			
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3	2		59.9	148	52	58	H [37]			
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	2	1		72.9	147	125	134	H [37]			
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	1	0		71.2	144	122	131	H [37]			
UO <sub>2</sub> (OH) <sub>2</sub>	1	0		51.4	135	28	34	H [37]			
UO <sub>2</sub> Br <sub>2</sub>	3	1		59.2	144	55	62	H [37]			
UO <sub>2</sub> Br <sub>2</sub>	1	0		76.7	144	155	164	H [37]			
UO <sub>2</sub> Cl <sub>2</sub>	3	1		60.7	149	54	61	H [37]			
UO <sub>2</sub> Cl <sub>2</sub>	1	0		74.5	147	135	143	H [37]			

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## Appendix A (continued)

Salt	H	L	(E/V) (GJ/m <sup>3</sup> )	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol·K))	$T_{hy}$ (°C)	$T_{deh}$ (°C)	Source	$T_{min}$ (K)	$T_{max}$ (K)	Comment
UO <sub>2</sub> F <sub>2</sub>	3	0		51.8	144	16	22	H [37]			
UO <sub>2</sub> SO <sub>4</sub>	3.5	3		58.4	164	21	26	H [37]			
UO <sub>2</sub> SO <sub>4</sub>	3	2.5		47.2	133	8	13	H [37]			*
UO <sub>2</sub> SO <sub>4</sub>	2.5	1		77.0	141	164	174	H [37]			
UO <sub>3</sub>	2	1		47.3	135	5	11	H [37]			*
UO <sub>3</sub>	1	0.9		71.4	106	226	239	H [37]			
UO <sub>3</sub>	0.9	0		72.1	156	102	109	H [37]			
UOF <sub>2</sub>	1	0		55.6	147	31	37	H [37]			
UOFOH	0.5	0		57.0	145	42	48	H [37]			
V <sub>2</sub> O <sub>5</sub>	1	0		52.2	147	14	19	H [37]			
VOSO <sub>4</sub>	6	5	0.38	52.0	149	11	16	H [37]			
VOSO <sub>4</sub>	5	3	0.93	56.9	149	35	40	H [37]			
VOSO <sub>4</sub>	3	1	1.35	64.3	149	73	80	H [37]			
VOSO <sub>4</sub>	1	0	1.86	134.7	149	498	517	H [37]			
YbCl <sub>3</sub>	6	0		12.3	147	75	75	H [37]			*
YbPO <sub>4</sub>	2	0		113.8	151	361	375	H [37]			
YCl <sub>3</sub>	6	0	2.84	73.6	149	125	133	H [37]			*
YPO <sub>4</sub>	2	0		50.7	149	5	9	H [37]			*
Zn(ClO <sub>4</sub> ) <sub>2</sub>	6	4	0.13	11.0	−4	92	135	pT [36]	373	533	*
Zn(NO <sub>3</sub> ) <sub>2</sub>	6	4	0.86	62.1	167	34	39	H [37]			
Zn(NO <sub>3</sub> ) <sub>2</sub>	6	2				34	93	Com			
Zn(NO <sub>3</sub> ) <sub>2</sub>	6	0				34	104	Com			
Zn(NO <sub>3</sub> ) <sub>2</sub>	4	2	0.91	52.6	111	84	93	H [37]			
Zn(NO <sub>3</sub> ) <sub>2</sub>	4	0				84	104	Com			
Zn(NO <sub>3</sub> ) <sub>2</sub>	2	0	1.61	71.5	157	96	104	H [37]			
ZnBr <sub>2</sub>	2	0	1.44	62.3	159	46	52	H [37]			
ZnF <sub>2</sub>	4	0	2.92	55.7	151	26	31	H [37]			
ZnSO <sub>4</sub>	7	6	0.39	57.2	160	19	25	pT [92]	301	309	
ZnSO <sub>4</sub>	7	6	0.40	59.4	164	26	31	H [37]			
ZnSO <sub>4</sub>	6	2	1.65	53.5	146	22	28	H [37]			
ZnSO <sub>4</sub>	6	1	2.00	52.1	141	21	27	pT [36]	291	305	
ZnSO <sub>4</sub>	2	1	0.83	49.6	135	18	24	H [37]			
ZnSO <sub>4</sub>	1	0	1.55	82.6	161	148	157	H [37]			

Appendix B. K<sub>2</sub>CO<sub>3</sub>

Fig. 8 shows the phase diagram of K<sub>2</sub>CO<sub>3</sub>–H<sub>2</sub>O based on several sources. Some discrepancy between the different sources is visible: the dihydrate of Lescouer [36] is not observed by other researchers and the corresponding phase equilibrium line is similar to the sesquihydrated K<sub>2</sub>CO<sub>3</sub>. Based on our own measurements with K<sub>2</sub>CO<sub>3</sub> (supplier Sigma-Aldrich), we expect that the dihydrate is a misinterpretation of the observed sesquihydrate by Lescouer. In addition, the transition based on the data of Glasser (the 0.5–0) is not observed in our experiments as well. Recent insights point towards a single 0–1.5 transition, also observed by Stanish and Perlmutter [93]. This reduces the dehydration temperature and complexity of the TCM-reaction. Based on the extrapolated deliquescence line in Fig. 8, deliquescence of this material is not expected under working conditions.

We conclude with kinetic data of K<sub>2</sub>CO<sub>3</sub>, reported by Stanish and Perlmutter [69,94,93,95]. They analyzed the effect of the grain size, applied vapor pressure and temperature on the reaction rate. Also some first cyclic experiments were performed in which they indicate a hydration rate influenced by dehydration conditions

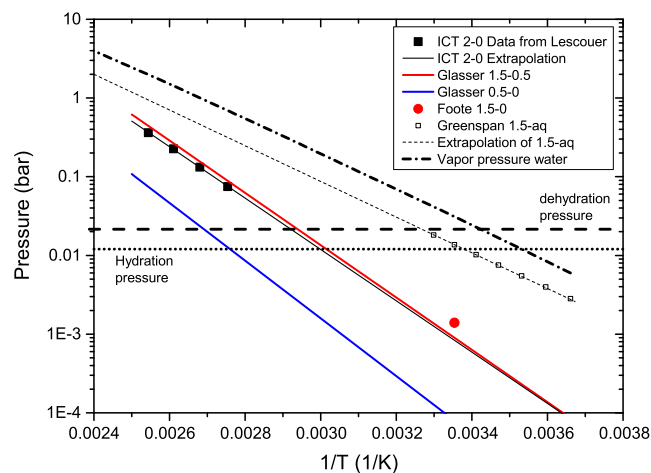


Fig. 8. The phase diagram of K<sub>2</sub>CO<sub>3</sub> in equilibrium with water. The data are a combination of experimental and calculated data from the literature, i.e., Lescouer [36], Glasser [38], Foote [96] and Greenspan [54].

and the number of cycles of the material. Their results indicate that the composed phase diagram is correct within the expected errors.

## Appendix C. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apenergy.2017.04.080>.

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