

Article

# Thermodynamic Efficiency of Water Vapor / Solid Chemical Sorption Heat Storage for Buildings: Theoretical Limits and Integration Considerations

Frédéric KUZNIK<sup>1</sup> <sup>1</sup> Université de Lyon, INSA-Lyon, CETHIL UMR5008 F-69621, Villeurbanne, France;

frederic.kuznik@insa-lyon.fr

**Featured Application:** The paper provides theoretical limits of chemisorption heat storage in buildings and also discusses solutions for an efficient system integration.

**Abstract:** The theoretical limits of water sorbate based chemical sorption heat storage are investigated in this study. First, a classification of *thermochemical heat storage* is proposed based on bonding typology. Then, thermodynamics of chemical solid/gas sorption is introduced. The analysis of the reaction enthalpy from the literature indicates that this value is only slightly varying for one mole of water. Using this observation, and with the help of thermodynamical considerations, it is possible to derive conclusions on energy efficiency of closed and open heat storage systems. Whatever the salt, the main results are 1) the energy required for evaporation of water is, at least, 65% of the available energy of reaction and 2) the maximum theoretical energy efficiency of the system is about 1.8.

**Keywords:** Chemical sorption; Heat storage; System efficiency; Reaction enthalpy; Theoretical limits

## 1. Introduction

It is obvious that everything has a limit. However it is better to know its value in order to avoid wasting effort to find means of going beyond that limit ! Chemical solid/gas sorption has a relatively high potential of heat storage density and is a subject of interest to both scientists and engineers [1–8]. Among possible reactants, water sorbate based chemical reactions have retained attention because of non-toxicity and availability of water. Whatever the system, closed or open reactor, one of the main design criteria is the energy efficiency of the thermal storage system. In the present work, only reactions involving temperatures below 150 °C are considered, which corresponds to a building application [1]. However, the ideas developed in the present paper can be straightforward adapted to other applications or other sorbates.

MgCl<sub>2</sub> · 6 H<sub>2</sub>O was selected by [9] to be tested in a 17 L open reactor. Under realistic operating condition, the energy storage capacity of the reactor reached about 139 kWh m<sup>-3</sup>. The energy efficiency was characterized by the instantaneous electrical COP of the system evaluated via:

$$COP_{el} = \frac{P_{heating}}{P_{fan}} \quad (1)$$

where  $P_{heating}$  is the heat released and  $P_{fan}$  the fan electrical energy. An instantaneous electrical COP of 12 was found, but the authors expected to reach up to 30 with an optimization of heat recovery and pressure drop in the system. Of course this high COP value is a direct consequence of its "home-made" definition. For the sake of clarity, the present study will only deals with thermodynamics efficiency of the system.

A lab-scale closed thermochemical heat storage reactor was developed in [10], capable of holding about 974 g of material. The storage material used was SrBr<sub>2</sub> · 6 H<sub>2</sub>O and 13 dehydration-hydration

29 cycles were conducted. The energy storage capacity of the reactor was about 65 kWh. The reactor  
30 thermal energy efficiency is 0.77 meaning a global heat loss of 23%.

31 It is worth mentioning that other reactors have been experimentally tested but no data are  
32 available concerning the energy efficiency:

- 33 •  $\text{SrBr}_2 \cdot 6 \text{H}_2\text{O}$  in an open reactor – [11],
- 34 •  $\text{Na}_2\text{S} \cdot 5 \text{H}_2\text{O}$  in a closed reactor – [12],
- 35 •  $\text{SrBr}_2 \cdot 6 \text{H}_2\text{O}$  in an open reactor – [13,14],
- 36 •  $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$  in a closed reactor – [15],
- 37 •  $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$  in an open reactor – [16].

38 The experimental investigation was focused on the reactor alone and the storage capacity and  
39 efficiency were based on a perfect system integration. For example, heat required for water vapor  
40 generation is never evaluated nor discussed.

41 On the other side, the theoretical COP of chemical heat pump, i.e. closed system, was studied  
42 in [17]. Calculated standard enthalpy of reaction of 34 salts were used to evaluate the influence  
43 of thermophysical properties on energy and exergy efficiency of a perfect system with recovery of  
44 condensation heat and "energy-free" heat of vaporization. The main results were 1) the maximum  
45 COP is about 1.84 for  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  and 2) the behavior of the energetic efficiency and the exergetic  
46 efficiency is opposite. The calculations were based on the evaluation of the perfect thermodynamic  
47 cycle.

48 We propose, in this paper, to evaluate the theoretical limits of the thermodynamic efficiency of  
49 water sorbate / salt chemical sorption heat storage system. To our knowledge, it is the first attempt  
50 to evaluate such limits. The starting point of our work is simple: regarding data from the literature,  
51 the enthalpy of reaction of one mole of water varies little from one reaction to the other. Then, with  
52 the help of chemical thermodynamics, it is possible to derive general considerations concerning the  
53 efficiency of open and closed heat storage systems.

## 54 2. Classification of reaction heat storage

55 In the literature, *thermochemical heat storage* is employed for a family of reactions involving both,  
56 physical and chemical processes. A tentative of classification is given in [18] and is presented in  
57 Fig. 1. However, in this classification, sorption is used to integrate different physical phenomena  
58 and can lead to misunderstandings. Then, we propose, in this section, to derive a classification of  
59 thermochemical heat storage based on a physical phenomena typology. We deliberately limit the  
60 classification development to heterogeneous<sup>1</sup> reactions as homogeneous reactions are seldom used for  
61 thermal energy storage.

62 Let's first define sorption: according to [19], sorption is *the process by which a substance (sorbate) is*  
63 *sorbed (adsorbed or absorbed) on or in another substance (sorbent)*. The process can be caused by physical  
64 bonding, i.e. physical sorption, or chemical bonding, i.e. chemical sorption. The main difference  
65 between physical and chemical sorption lies in the nature of created bonds. Physical sorption is weak,  
66 long range bonding mostly Van der Waals interactions and hydrogen bonding. Chemical sorption is  
67 strong, short range bonding involving orbital overlap and charge transfer. Another main difference  
68 between physical and chemical sorption is that the latter requires activation energy whereas it is not  
69 the case for the first process.

70 Sorption can be absorption or adsorption. Definitions of both processes can be found in [19]:

- 71 • Absorption is *the process of one material (absorbate) being retained by another (absorbent); this may be*  
72 *the physical solution of a gas, liquid, or solid in a liquid, attachment of molecules of a gas, vapor, liquid, or*  
73 *dissolved substance to a solid surface by physical forces, etc.*

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<sup>1</sup> Involving components of two or more phases.

- 74 • Adsorption is an increase in the concentration of a dissolved substance at the interface of a condensed  
75 and a liquid phase due to the operation of surface forces. Adsorption can also occur at the interface of a  
76 condensed and a gaseous phase.

77 While molecule undergoing absorption are taken up through the bulk of the absorbent (for example  
78 by diffusion), adsorption is a surface process. It is sometimes difficult to find the difference between  
79 adsorption and absorption. Taking for example the dehydration of lithium sulphate monohydrate [20]  
80 (i.e. chemical sorption), nucleation is supposed to occur at the surface of the grain (adsorption) and  
81 then the growth proceeds towards the center of the grains by diffusion (absorption).

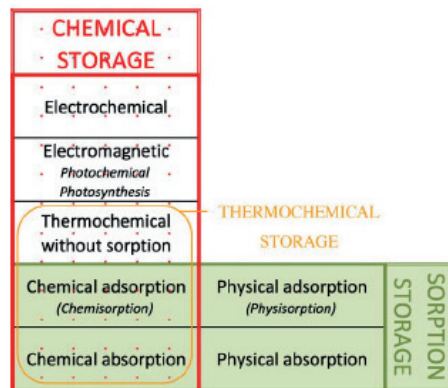


Figure 1. Chemical storage and sorption storage classification – extracted from [18].

82 Physical sorption can be split into absorption and adsorption:

- 83 • In physical absorption, the mass transfer takes place at the interface between the absorbate and  
84 the absorbent. This type of absorption depends on the solubility of absorbate, the pressure and  
85 the temperature. The rate and amount of absorption also depend on the surface area of the  
86 interface and its duration in time.
- 87 • Physical adsorption is called physisorption. Physisorption is *adsorption in which the forces involved*  
88 *are intermolecular forces (Van der Waals forces) of the same kind as those responsible for the imperfection*  
89 *of real gases and the condensation vapors, and which do not involve a significant change in the electronic*  
90 *orbital patterns of the species involved. The term van der Waals adsorption is synonymous with physical*  
91 *adsorption, but its use is not recommended.* [19].

92 Similarly to physical sorption, chemical sorption can be split into absorption and adsorption:

- 93 • Chemical absorption or reactive absorption is a chemical reaction between the absorbed and the  
94 absorbing substances. Sometimes it combines with physical absorption. This type of absorption  
95 depends upon the stoichiometry of the reaction and the concentration of its reactants.
- 96 • Chemical adsorption is called chemisorption. Chemisorption is *Adsorption which results from*  
97 *chemical bond formation (strong interaction) between the adsorbent and the adsorbate in a monolayer on*  
98 *the surface.* [19].

99 From the previous definition, we propose in Fig. 2 a classification of heat storage systems based on  
100 the physical/chemical phenomena involved. For heat storage, the split between physical and chemical  
101 sorption is important as the heat related to these reactions is quite different. For example, heat of  
102 adsorption is different for physisorption and chemisorption:

- 103 • Physisorption: 5 – 45 kJ mol<sup>-1</sup> in [21]; 2 – 29 kJ mol<sup>-1</sup> in [22]  
104 • Chemisorption: 80 – 400 kJ mol<sup>-1</sup> in [21]; > 30 kJ mol<sup>-1</sup> in [22]

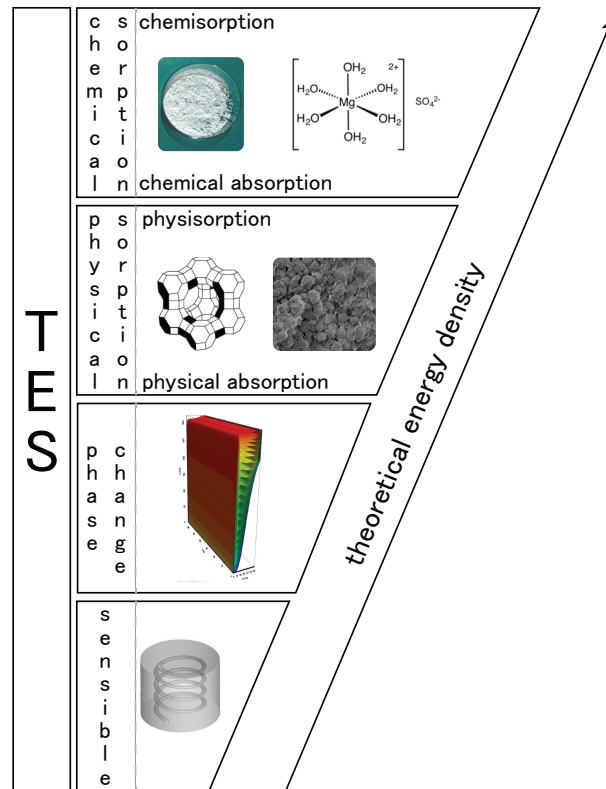
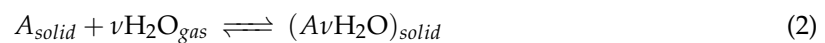


Figure 2. Classification of heat storage by physical phenomena.

### 105 3. Basics of chemical thermodynamics

#### 106 3.1. Energy change in chemical sorption

Let's consider the water sorbate heterogeneous chemical sorption reaction process expressed under the following general form:



The first law of thermodynamics states that the change in the internal energy of a system  $\Delta U$  is equal to the sum of the heat gained/lost by the system  $Q$  and the work done by/on the system  $W$ :

$$\Delta U = Q + W \quad (3)$$

The amount of work of expansion done by the reaction during any transformation is given by:

$$W = - \int P \times dV \quad (4)$$

At constant volume (i.e.  $W = 0$ ), the heat given off or absorbed by the reaction is equal to the change in the internal energy that occurs during the reaction:

$$\Delta U = Q_V \quad (5)$$

107 Such configuration is close to **closed chemical sorption heat storage systems**.

At constant pressure, the change in the internal energy occurring the reaction is given by:

$$\Delta U = Q_P + W = Q_P + P \times \Delta V \quad (6)$$

Let's introduce the enthalpy of the system  $H$  related to the internal energy by:

$$H = U + P \times V \quad (7)$$

Then, the heat given off or absorbed during a chemical reaction at constant pressure is equal to the change in the enthalpy of the system:

$$\Delta H = Q_p \quad (8)$$

108 Such configuration is close to **open chemical sorption heat storage systems**.

The relationship between the change in internal energy and the change in enthalpy, assuming an ideal gas, is given by:

$$\Delta H = \Delta U - \nu \times R \times T \quad (9)$$

109 where  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $\nu$  the stoichiometric coefficient defined in Eq. 2. For a temperature  
110 of 273.15 K,  $R \times T = 2.27 \text{ kJ mol}^{-1}$ . This value is very low compared to heat of reaction given per  
111 mole of water<sup>2</sup>, less than 4%, and then can be neglected. Consequently, it is possible to assume that the  
112 change in internal energy is more or less equal to the change in enthalpy.

### 113 3.2. Enthalpy of reaction

For the reaction given in equation 2,  $dn_{\text{H}_2\text{O}}$ ,  $dn_A$  and  $dn_{A\nu\text{H}_2\text{O}}$  are respectively the mole variation of water, solid  $A$  and solid  $A\nu\text{H}_2\text{O}$ . Then, the degree of advancement of the reaction  $\xi$  is given by:

$$d\xi = \frac{dn_{\text{H}_2\text{O}}}{\nu} = dn_A = dn_{A\nu\text{H}_2\text{O}} \quad (10)$$

The variation of enthalpy can be written under the following form:

$$dH = \left( \frac{\partial H}{\partial P} \right)_{T,\xi} \times dP + \left( \frac{\partial H}{\partial T} \right)_{P,\xi} \times dT + \Delta_r H \times d\xi \quad (11)$$

114 where  $\Delta_r H$  is the enthalpy of reaction at constant temperature and pressure. Of course, for  
115 a transformation at constant pressure and temperature<sup>3</sup>, the variation of enthalpy is given by  
116  $\Delta H = \Delta_r H \times \xi = Q_p$

117 The standard enthalpy of reaction (denoted  $\Delta_r H^0$ ) is the enthalpy change that occurs in a system  
118 when one mole of matter is transformed by a chemical reaction under standard conditions, i.e. a  
119 temperature of 273.15 K and a pressure of 100000 Pa. The standard enthalpy of reaction can be  
120 measured or computed using the standard enthalpy of formation of the reactants and products.

The enthalpy of reaction for a a temperature  $T$  is related to the standard enthalpy of reaction via:

$$\Delta_r H^0_T = \Delta_r H^0_{273.15} + \int_{273.15}^T (C_{A\nu\text{H}_2\text{O}} - C_A - \nu \times C_{\text{H}_2\text{O}}) \times dT \quad (12)$$

121 where  $C$  is the specific heat of  $A\nu\text{H}_2\text{O}$ ,  $A$  or  $\text{H}_2\text{O}$ . It is worth mentioning that, usually, the quantity

122  $\int_{273.15}^T (C_{A\nu\text{H}_2\text{O}} - C_A - \nu \times C_{\text{H}_2\text{O}}) \times dt$  is small compared to  $\Delta_r H^0_{273.15}$ .

<sup>2</sup> Values of enthalpies of reaction are given in table 1

<sup>3</sup> Constant temperature or neglected variation of enthalpy due to temperature change.

Hydrated salt	Dehydrated salt	$\Delta_r H$ [kJ mol <sup>-1</sup> ]	$\Delta_r H/\nu$ [kJ mol <sup>-1</sup> ]	Reference
MgSO <sub>4</sub> · 6 H <sub>2</sub> O	MgSO <sub>4</sub> · H <sub>2</sub> O	275.7	55.1	[27]
LiNO <sub>3</sub> · 3 H <sub>2</sub> O	LiNO <sub>3</sub>	165.8	55.3	[28]
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 18 H <sub>2</sub> O	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 8 H <sub>2</sub> O	554.5	55.4	[28]
CaCl <sub>2</sub> · 6 H <sub>2</sub> O	CaCl <sub>2</sub> · H <sub>2</sub> O	277.0	55.4	[28]
CuSO <sub>4</sub> · 5 H <sub>2</sub> O	CuSO <sub>4</sub> · 3 H <sub>2</sub> O	111.7	55.8	[27]
SrCl <sub>2</sub> · 6 H <sub>2</sub> O	SrCl <sub>2</sub>	342.0	57.0	[28]
LiSO <sub>4</sub> · H <sub>2</sub> O	LiSO <sub>4</sub>	57.2	57.2	[27]
CuSO <sub>4</sub> · 3 H <sub>2</sub> O	CuSO <sub>4</sub> · H <sub>2</sub> O	114.8	57.4	[27]
La(NO <sub>3</sub> ) <sub>3</sub> · 6 H <sub>2</sub> O	La(NO <sub>3</sub> ) <sub>3</sub> · 1.5 H <sub>2</sub> O	260.4	57.9	[28]
MgCl <sub>2</sub> · 6 H <sub>2</sub> O	MgCl <sub>2</sub> · 4 H <sub>2</sub> O	116.4	58.2	[27]
LaCl <sub>3</sub> · 7 H <sub>2</sub> O	LaCl <sub>3</sub> · H <sub>2</sub> O	355.5	59.3	[28]
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5 H <sub>2</sub> O	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	279.9	56.0	[28]
MgSO <sub>4</sub> · 7 H <sub>2</sub> O	MgSO <sub>4</sub> · H <sub>2</sub> O	335.7	56.0	[28]
CaCl <sub>2</sub> · 2 H <sub>2</sub> O	CaCl <sub>2</sub> · 0.3 H <sub>2</sub> O	101.0	59.4	[29]
MgCl <sub>2</sub> · 6 H <sub>2</sub> O	MgCl <sub>2</sub>	361.2	60.2	[30]
KOH · 2 H <sub>2</sub> O	KOH · 1.2 H <sub>2</sub> O	48.2	60.3	[28]
Zn(NO <sub>3</sub> ) <sub>2</sub> · 6 H <sub>2</sub> O	Zn(NO <sub>3</sub> ) <sub>2</sub>	372.0	62.0	[28]
Na <sub>2</sub> S · 5 H <sub>2</sub> O	Na <sub>2</sub> S	310.0	62.0	[31]
CaBr <sub>2</sub> · 6 H <sub>2</sub> O	CaBr <sub>2</sub> · 0.3 H <sub>2</sub> O	353.9	62.1	[28]
LiCl · H <sub>2</sub> O	LiCl	62.2	62.2	[28]
K <sub>2</sub> CO <sub>3</sub> · 1.5 H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	95.5	63.7	[28]
SrBr <sub>2</sub> · 6 H <sub>2</sub> O	SrBr <sub>2</sub> · H <sub>2</sub> O	337.0	67.4	[28]
MgCl <sub>2</sub> · 4 H <sub>2</sub> O	MgCl <sub>2</sub> · 2 H <sub>2</sub> O	135.6	67.8	[27]

**Table 1.** Measured enthalpy of reaction extracted from the literature.

Moreover, the chemical sorption reaction being monovariant, the equilibrium is given by the Clausius–Clapeyron relation:

$$\ln \left( \frac{P_e}{P_0} \right) = -\frac{\Delta_r H^0}{\nu \times R \times T_e} + \frac{\Delta_r S^0}{\nu \times R} \quad (13)$$

123 where  $P_e$  is the equilibrium water vapor pressure [Pa] and  $T_e$  the equilibrium temperature [K].

#### 124 4. Material considerations

125 In the remaining of the study, we will consider only reactions involving temperatures below  
126 150 °C which corresponds to a building application [1]. However, the ideas developed in the present  
127 paper can be straightforward adapted to other applications or other sorbates.

128 The dehydration of cobalt(II) chloride–6–hydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O) was investigated in [23]. The  
129 enthalpy of formation was calculated using thermodynamic values. The results show that one mole of  
130 water corresponds to a variation of the reaction enthalpy about 55.2 kJ mol<sup>-1</sup>. It is worth mentioning  
131 that the latter value is very close to the enthalpy of vaporization of ice at 25 °C i.e. 52 kJ mol<sup>-1</sup>. This  
132 conclusion is also validated by [24].

133 Enthalpy of reaction given in the literature are summarized in table 1. The main result is that the  
134 enthalpy of reaction of one mole of water only varies between 55.1 kJ mol<sup>-1</sup> and 67.8 kJ mol<sup>-1</sup>. Of  
135 course, this value is close to the observations made in the literature and given above. This specific  
136 feature is the basis of the system maximum theoretical efficiency limits.

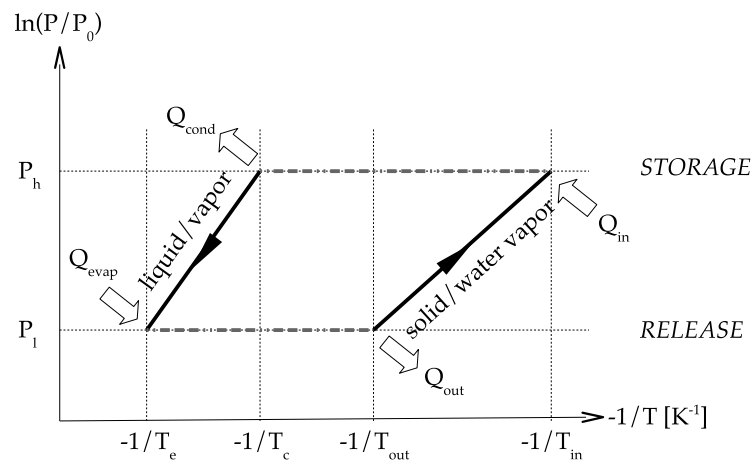


Figure 3. Theoretical Clausius–Clapeyron chemical sorption cycle.

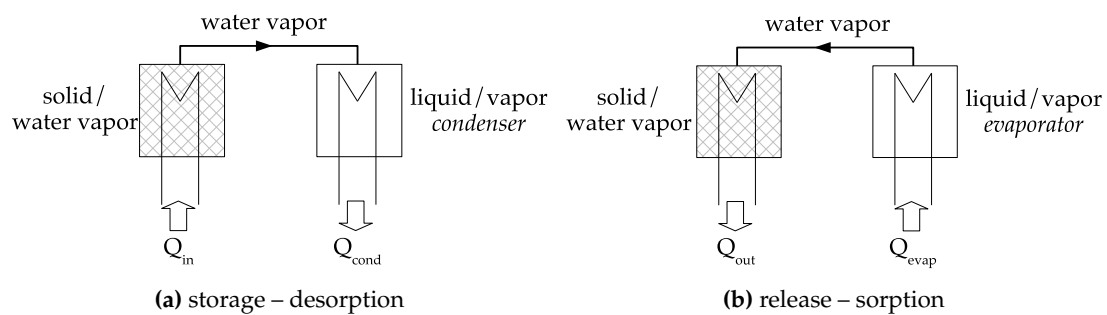


Figure 4. Closed heat storage system – quantities refer to Fig. 3.

## 137 5. System efficiency

### 138 5.1. Concepts

139 The schematic diagram of a perfect sorption thermal battery for energy storage using solid–water  
 140 vapor chemical reaction is presented in Fig. 3. The two curves present the solid/water vapor  
 141 equilibrium of the sorbent and the vapor/liquid equilibrium of the water sorbate. Under the  
 142 solid/water vapor line, the sorbent is under the  $A_{solid}$  form. Above the solid/water vapor line,  
 143 the sorbent is under the  $(AvH_2O)_{solid}$  form. Basically, the two main concepts of system design are  
 144 closed and open.

145 The principle of a closed chemical sorption heat storage system is given in Fig. 4. Initially, sorbent  
 146 is under the  $(AvH_2O)_{solid}$  form. During the storage phase,  $Q_{in}$  heat is transferred to the material at the  
 147 temperature  $T_{in}$ . Then, the water vapor pressure is increasing and the gas moves from the material  
 148 to the condenser where the pressure is  $P_h$ . Then, the vapor condensates<sup>4</sup> and heat of condensation is  
 149 released,  $Q_{cond}$ . During the release phase, liquid is evaporated<sup>5</sup> at temperature  $T_e$ , requiring a quantity  
 150 of heat,  $Q_{evap}$ . As pressure is higher in the evaporator than in the material, a gas flow occurs. A  
 151 quantity of heat  $Q_{out}$  is then released during the sorption process in the material.

152 The other option lies in the use of an open system, presented in Fig. 5. The idea is to use a carrier  
 153 inert gas and sorbate mixing, typically dry air and water vapor (i.e. humid air). During the storage

<sup>4</sup> in the condenser

<sup>5</sup> in the evaporator

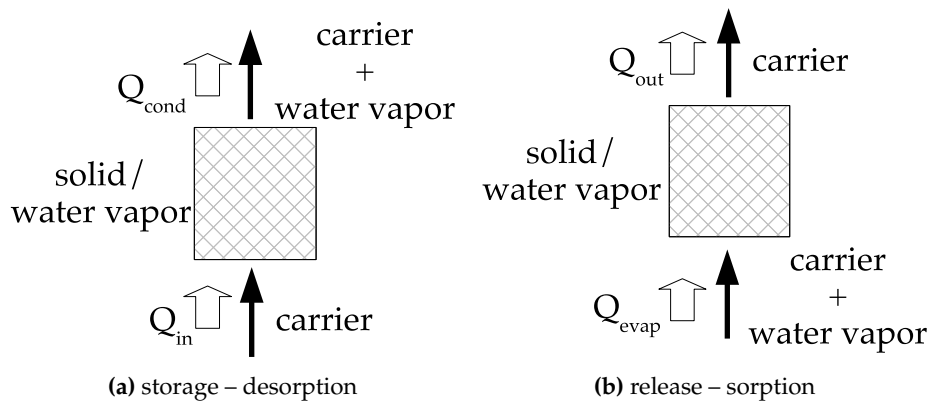


Figure 5. Open heat storage system – quantities refer to Fig. 3.

154 phase, the carrier (or the mixing) is passing through the material under the  $(AvH_2O)_{solid}$  form.  $Q_{in}$   
 155 heat is then transferred to the material at the temperature  $T_{in}$ , resulting in the desorption process  
 156 and a potential heat of condensation in the carrier,  $Q_{cond}$ . During the release phase, the mixing is  
 157 passing through the material under the  $A_{solid}$  form and may requires a quantity of heat to evaporate  
 158 liquid water,  $Q_{evap}$ . The water vapor is sorbed and heat is  $Q_{out}$  heat is transferred to the carrier (or the  
 159 mixing).

## 160 5.2. Thermodynamic Efficiency

161 Whatever the system open or closed, it is important to answer the issue related to the  
 162 thermodynamic efficiency limit of the heat storage. Basically, the designer of such system must  
 163 know the thermodynamics limit to evaluate the enhancement possibilities of its prototype.

Let's first define  $Q^+$  as the supplied energy per mole of salt to the storage system and  $Q^-$  as the  
 recovered energy per mole of salt. The efficiency of the system  $\eta$  is defined, for the sake of universality,  
 as:

$$\eta = \frac{Q^-}{Q^+} \quad (14)$$

164 This efficiency can also be found as COP in the literature [3]. However, the definition of COP may  
 165 vary from an author to the other: an example is the definition of COP given by [9] which is completely  
 166 different from the one given by [17].

167 The maximum reachable efficiency  $\eta_{max}$  is calculated with the maximum  $Q^-$ , called  $Q_{max}^-$ , and, of  
 168 course, the minimum  $Q_{min}^+$ .

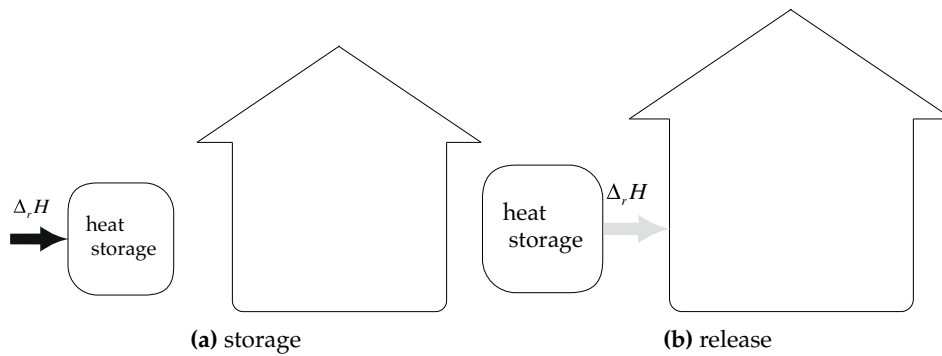
169 The assumptions used to evaluate the **theoretical limits** of the energy efficiency are:

- 170 ○ Heat losses in the system are not taken into account.
- 171 ○ Sensible heat of materials and parts of the reactor are neglected.
- 172 ○ The energy taken off or absorbed by the reaction is approximated by the standard enthalpy of  
 173 reaction.
- 174 ○ The equilibrium drop influence is neglected (see [17]).
- 175 ○ Only total hydration / dehydration processes are considered.

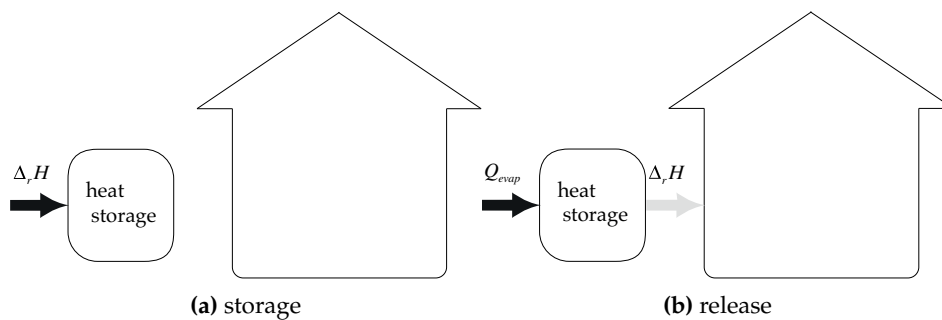
176 Given the previous assumptions, if the heat of condensation is not recovered and if the heat of  
 177 evaporation is energy-free<sup>6</sup>, the trivial efficiency is  $\eta_{max} = 1$  (see Fig. 6 –  $Q_{max}^- = Q_{min}^+ = \Delta_r H^0$ ).

<sup>6</sup> Energy-free means that no additional energy is required for producing water vapor.





**Figure 6.** System integration: heat of condensation is not recovered and heat of evaporation is energy-free:  $\eta_{max} = 1$ .



**Figure 7.** System integration: heat of condensation is not recovered and heat of evaporation is not free:  $\eta_{max} = \frac{1}{1 + \frac{Q_{evap}}{\Delta_r H^0}}$ .

Considering the previous assumptions, if non-free heat of evaporation, the maximum efficiency becomes (see Fig. 7):

$$\eta_{max} = \frac{Q_{max}^-}{Q_{min}^+} = \frac{\Delta_r H^0}{\Delta_r H^0 + Q_{evap}} = \frac{1}{1 + \frac{Q_{evap}}{\Delta_r H^0}} \quad (15)$$

The quantity of energy required to evaporate liquid water per mole of salt is evaluated with:

$$Q_{evap} = \nu \times M_{H_2O} \times L_v \quad (16)$$

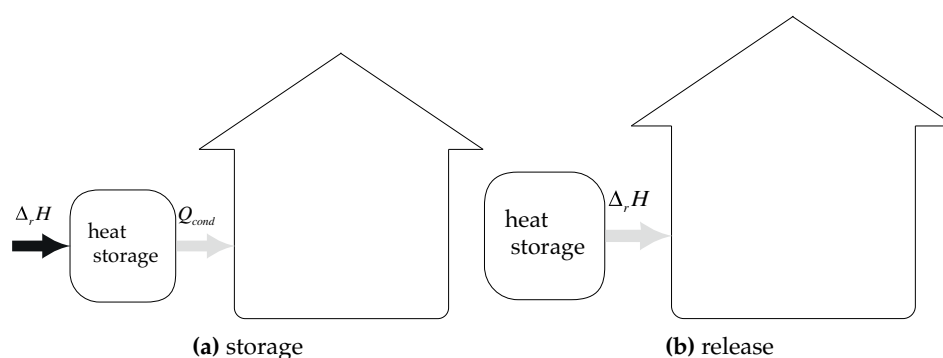
where  $L_v$  is the water heat of vaporization in standard conditions taken as  $2456 \text{ kJ kg}^{-1}$  and  $M_{H_2O}$  the molar mass of water equal to  $18 \text{ g mol}^{-1}$ . Considering data from table 1, and considering that  $\Delta_r H^0 / \nu$  is few varying from one salt to another, the ratio  $Q_{evap} / \Delta_r H^0$  can be evaluated as:

$$0.65 \leq \frac{Q_{evap}}{\Delta_r H^0} \leq 0.80 \quad (17)$$

178 The previous equation also shows that energy required for evaporation is, at least, 65% of the  
179 **available energy of reaction!** The maximum energy efficiency of the integrated system  $\eta_{max}$  is then  
180 varying between 55% and 60% only.

Let's now consider the case with a total recover of condensation heat and free-energy heat of evaporation. Then, the energy efficiency becomes (see Fig. 8):

$$\eta_{max} = \frac{Q_{max}^-}{Q_{min}^+} = \frac{\Delta_r H^0 + Q_{cond}}{\Delta_r H^0} = 1 + \frac{Q_{cond}}{\Delta_r H^0} \quad (18)$$



**Figure 8.** System integration: heat of condensation is recovered and heat of evaporation is energy-free:  $\eta_{max} = 1 + \frac{Q_{cond}}{\Delta_r H^0}$ .

The quantity of energy (per mole of salt) recoverable from condensation is evaluated by:

$$Q_{cond} = \nu \times M_{H_2O} \times L_v \quad (19)$$

Then, the energy efficiency of the system is evaluated via the simple equation:

$$1.6 \leq \eta_{max} \leq 1.8 \quad (20)$$

181 The maximum theoretical energy efficiency of the system is about 1.8, whatever the salt! This  
 182 conclusion is clearly in accordance with the results of [17] where the maximum value is 1.84. However,  
 183 our study extends these results to the integration of an open system.

## 184 6. Conclusions

185 Regarding data from the literature, the reaction enthalpy of one mole of water only varies between  
 186  $55.1 \text{ kJ mol}^{-1}$  and  $67.4 \text{ kJ mol}^{-1}$ . Considering an open or closed single-stage system, the two main  
 187 conclusions are:

- 188 • Energy required for evaporation of water is, at least, 65% of the available energy of reaction.
- 189 • For a perfect system, the maximum theoretical energy efficiency of the system is about 1.8.

190 The previous conclusions don't depend on the adsorbent material considered. Then, a special  
 191 attention must be paid from a system point of view for:

- 192 • Developing water evaporation system "energy-free" or low-energy for the discharging phase.
- 193 • Developing or using water condensation recovering systems: examples of such recovering  
 194 systems are the cascaded thermal battery [25,26] or the integration of a heat-pump.

195 Of course, these theoretical limits remain valid for the operating conditions given in this work  
 196 and further studies must be carried to extend the conclusions to higher temperature storage. Moreover,  
 197 numerical modeling is also under investigation to evaluate the potential improvement of the system  
 198 integrated in the building.

199 **Conflicts of Interest:** The author declares no conflict of interest.

200 **List of symbols****LIST OF SYMBOLS**

$C$	specific heat capacity	$\text{J kg}^{-1} \text{K}^{-1}$
$H$	enthalpy	$\text{J}$
$L_v$	vaporization heat of water	$\text{J kg}^{-1}$
$P$	pressure	$\text{Pa}$
$Q$	heat energy per mole of salt	$\text{J mol}^{-1}$
$R$	gas constant	$\text{J K}^{-1} \text{mol}^{-1}$
$S$	entropy	$\text{J}$
$T$	temperature	$\text{K}$
$U$	internal energy	$\text{J}$
$V$	volume	$\text{m}^3$
$W$	work	$\text{J}$

*Greek letters*

201 $\nu$	stoichiometric coefficient
$\eta$	efficiency
$\xi$	advancement of reaction

*Subscript*

$e$	equilibrium
$evap$	evaporation
$max$	maximum
$min$	minimum
$r$	reaction
0	standard

*Superscript*

0	standard
–	recovered energy
+	supplied energy

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