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Thermal Operation Maps for Lamm–Honigmann Thermo-Chemical Energy Storage—A Quasi-Stationary Model for Process Analysis [†]

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Abstract: The Lamm–Honigmann energy storage is a sorption-based storage that can be arbitrarily charged and discharged with both heat and electrical power. The mechanical charging and discharging processes of this storage are characterized by an internal heat transfer between the main components, absorber/desorber and evaporator/condenser, that is driven by the working-fluid mass transferred between those components with the help of an expansion or compression device, respectively. In this paper, thermal operation maps for the mechanical charging and discharging processes are developed from energy balances in order to predict power output and storage efficiency depending on the system state, which, in particular, is defined by the mass flow rate of vapor and the salt mass fraction of the absorbent. The conducted method is applied for the working-fluid pair LiBr/H₂O. In a first step, a thermal efficiency is defined to account for second-order losses due to the internal heat transfer; e.g., for discharging from a salt mass fraction of 0.7 to one of 0.5 (kg LiBr)/(kg sol.) at a temperature of 130 °C, it is found that the reversible shaft work output is reduced by 1.1–2.9%/(K driving temperature difference). For lower operating temperatures, the reduction is larger; e.g., at 80 °C, the efficiency loss due to heat transfer rises to 3.5%/K for a salt mass fraction of 0.5 (kg LiBr)/(kg sol.). In a second step, a quasi-stationary assumption leads to the thermal operation map from which the discharging characteristics can be found; e.g., at an operating temperature of 130 °C for a constant power output of 0.4 kW/m² heat exchanger area at volumetric and inner machine efficiencies of $\eta_i = \eta_{vol} = 0.8$ and for an overall heat-transfer coefficient of 1500 W/(K m²), the mass flow rate has to rise continuously from 1.5 to 4.2 g/(s m²), while the thermal efficiency is reduced from 97% to 83% due to this rise and due to the dilution of the sorbent. For this discharging scenario, the corresponding discharge time is 4.4 (min·m²)/(kg salt). This results in an exergetic storage density of around 29 Wh/(kg salt mass). For a charge-to-discharge ratio of 2 (charging times equals two times discharging time) and with the same heat-transfer characteristic and machine efficiencies for constant power charging with adiabatic compression, the system is charged at around 0.75 kW/m², resulting in a round-trip efficiency of around 27%. Besides those predictions for arbitrary charging and discharging scenarios, the derived thermal maps are especially useful for the dimensioning of the storage system and for the development of control strategies. It has to be noted that the operation maps do not illustrate the transient behavior of the system but its quasi-stationary state. However, it is shown, mathematically, that the system tends to return to this state when disturbed.

Keywords: thermochemical energy storage; absorption storage; storage and conversion; Carnot battery; thermal operation map; control strategy; storage efficiency; storage capacity



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1. Introduction

Energy storage plays a key role in decarbonizing energy systems relying on renewable sources. The Lamm–Honigmann process (LAHMA) is a thermo-chemical energy conversion and storage process that was originally invented to drive fireless locomotives. Patents were issued in the 19th century for the working-fluid pairs caustic soda and ammonia

water: Moritz Honigsmann in 1883/1885 [1,2] and Emile Lamm in 1870 [3]. The process is based on the principle of vapor-pressure depression of an un-loaded ad-/absorbent, compared to the pure working fluid. The stored energy can be retrieved in the form of heat, cold or also mechanical work [4]. The combination of storage and conversion renders the process unique and favorable for an optimized use of transient renewable energy and waste heat.

This paper investigates the storage concept with the in- and output of mechanical energy. In this configuration, the storage can be classified as a Carnot battery (CB). A CB describes a system in which electric energy is stored in a thermal-storage medium and discharged with the help of a classic heat-conversion cycle, whose efficiency limit is described by the well-known Carnot efficiency. The ideal CB, in this manner, consists, for charging, of a reversible heat pump isothermally receiving heat from a low-temperature reservoir (the thermal-storage medium for concepts storing cold) and isothermally rejecting heat to a high-temperature reservoir (the thermal-storage medium for concepts storing heat) and for discharging, of a reversible heat engine isothermally receiving heat from and isothermally rejecting heat to those reservoirs that, each, stay at the same temperature. The resulting ideal (1st order) round-trip efficiency of this Pumped Thermal Electricity Storage (PTES) is, consequently, 100% [5]. The theoretically achievable high round-trip efficiencies, the possibly low cost of storage media and the site-independency and long life-time of the installation make PTES very promising for the medium- to long-term bulk storage of transient renewable energies in stationary applications.

In recent years, different CB concepts have been discussed in the literature on theoretical and experimental bases. They vary in the heat-pump and heat-conversion cycles applied, the thermal-storage media used and the temperature levels they worked with. Brayton cycle, organic Rankine cycle (ORC) and cryo-process-based CBs have been investigated a lot in recent years and partly brought to or near to commercial applications. In [6], a state-of-the art review with comparison of different CB types and their market potential is given. An extensive review on CBs industrial applications and state of commercialization can be found in [7].

Brayton-cycle-based PTESs have mostly been investigated with the working fluids Argon or CO₂. To the authors' knowledge, experimental realizations have not been reported in journal publications, but demonstration facilities have been realized by companies, and grid-scale applications are currently being constructed (e.g., by 1414Degrees [8] and Stiesdal [9]). Recent academic publications have dealt with techno-economic analyses [10–12], efficiency [13] and multi-criterial configuration optimization [14], transient behavior and off-design studies [15,16], and system operation strategies [17,18], including combined heat, cold and power generation [19]. The thermal-storage medium is favorably sensible (or a working-fluid mixture with a continuous temperature glide during phase change) in order to match the temperature profiles of the working fluid and the storage.

For ORC-based cycles, single-component PCMs are preferably used as storage media for the same reason. Common synthetic and natural refrigerants are used as working fluids. Commercial applications are currently being developed by different companies; e.g., MAN [20,21] and Energydome [22] have running pilot plants in the MW range. Academics, in recent years, have conducted numerical investigations for their integration into subordinated energy systems/sector coupling [23–25]; for the choice of suitable (low-GWP) working fluids and as basis for test rig designs [26,27]; and for the analysis of economic design aspects [28] and part-load behavior [29]. Furthermore, lab-scale experiments have been conducted with 10 kW [30,31] and 840 W max. power output [32]. A review on ORC-based CBs was recently presented in [33].

A high technological readiness level among CBs is reached by liquid–air energy storages (LAESs). A commercial installation with a 50 MW power output is currently being realized in the UK by the company Highview Power (e.g., see [34]) and is planned to go into operation in 2023. Academics, therefore, focus on exergo-economic optimization (e.g., [35,36]) and integration into the energy system and industries (e.g., [37–39]).

The LAHMA storage differs from most of the CB concepts presented in the literature in the manner that it works on a single arbitrary temperature level (compare Figure 1). Therefore, its theoretical efficiency does not necessarily rise with the temperature of the storage material, as it is in the case of other PTES types, given that the low-temperature reservoir remains at the same temperature (a detailed analysis of this effect is given in [40]). The high- and low-enthalpy reservoirs are, in the first order, at the same temperature level, and the enthalpy difference of the storage reservoirs, in fact, arises from the physical bonding characteristics of the sorbate/sorbent pair. This said, the operation of the system near ambient temperature is, from the thermodynamic point of view, advantageous, as it eliminates self-discharge and usually reduces equipment costs. On the other hand, the working fluids' gas density reduces with temperature, making components larger. An economic optimum depending on working fluids exists.

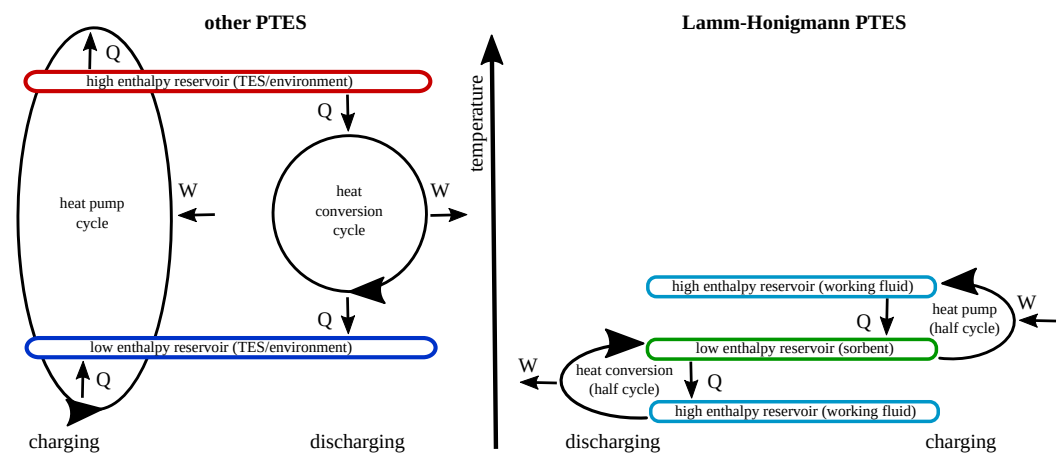


Figure 1. Schematic comparison of temperature levels of the high- and low-enthalpy reservoirs in LAHMA energy PTES compared to another PTES including driving temperature differences for the heat transfers.

Despite those thermodynamic advantages, the LAHMA (sorption-based) PTES has rarely been investigated in the last century (for more detailed historical background refer to, e.g., [41]). However, recent experimental work by Jahnke [42] has proven the potential of the process to be used as stationary energy storage.

In [42], Jahnke focuses on the plausibility of the experimental results and on the identification of the peculiarities of the prototype (e.g., heat losses, thermal masses, chosen process configuration, the inefficient expansion device). Those peculiarities are not necessarily representative of the general concept, but their influence on the figures of merit is large. Thus, the efficiency of the conversion of thermal to mechanical energy and the storage density were low (0.2% compared with the calculated 13% conversion efficiency and 0.2 Wh/kg compared with 12 Wh/kg if the expansion device worked isentropically and the thermal heat losses were neglected), but the reasons could be identified and the adaption of the experimental set-up is work in progress.

In the experiments, LiBr/H₂O was used as the working-fluid pair. It is well-known from absorption refrigeration applications, which have made it an attractive candidate for lab-scale experiments on the LAHMA storage. Still, the system was operated at a temperature of 130 °C (corrosion issues prevent it from going to higher temperatures), where the water vapor density is low.

Therefore, in [43] the author investigates the theoretical efficiencies of the storage system for other storage materials. The predicted round-trip efficiencies for the storage of mechanical work when charging nearly isothermally and discharging isentropically were 45% for the working pair Zeolith/H₂O and Silicagel/H₂O and 62% for NH₃/H₂O, compared with 48% for LiBr/H₂O at a storage temperature of 100 °C with an expansion and compression machine efficiency of 85%, respectively, and a driving temperature difference

of 5 K. The applied method allows a quick screening to be conducted before engaging detailed process analyses but lacks applicability to different discharging scenarios in terms of arbitrary power output. Due to the instationarity of the process, the results of the study are only applicable for narrow salt-mass-fraction ranges. However, for a large storage density, the change in mass fraction should be large. Furthermore, the dependency of the mass flow rate on the heat-transfer characteristics was not addressed.

As the vapor mass flow rate depends on the internal heat transferred, it also depends on the driving temperature difference for that internal heat transfer. Moreover, the value of the driving temperature difference, together with the sorbate mass fraction in the sorbent, influences the potential power output/required power input of the storage, as already analyzed in [43]. Thus, for the prediction of an arbitrary power output, this interdependency between the thermal and the mechanical systems has to be taken into account. While this was performed (for mechanical discharging only) in dynamic simulations in [44], for a specific expansion device delivering a specific mass flow rate (in this case, a turbine delivering a mass flow rate depending on the pressure ratio between evaporator and absorber), the present study focuses on the thermal interdependency for an arbitrary mass flow rate (and thus for arbitrary power out- and input).

A partial differential equation, describing the main driving forces within the process, is derived. By applying a quasi-stationary assumption, the process of mechanical charging and discharging can be explicitly described by a small set of equations without the need of integration. This helps to obtain a more general and fundamental understanding of the system, independent of its dedicated realization (e.g., size, working-fluid pair, temperature level, configuration, expansion/compression device used, starting conditions); therefore, it enables general system analysis and optimization to be conducted. Furthermore, the method can be used to develop operation control strategies and to dimension the storage system according to its application.

The equations are applied for the working-fluid pair LiBr/water, and important storage characteristics are obtained from the results.

2. Materials and Methods

2.1. Storage-Cycle Description

As already mentioned, the LAHMA storage concept has different realizations depending on the form of energy to store or extract. For a detailed description of thermal charging and discharging refer to, e.g., [4,43]. The basic system consists of a water heat exchanger (HX), which can work either as a condenser (C) or as an evaporator (E), and a solution HX, which can work as an absorber or as a desorber. The mechanical charging and discharging processes are shown in Figure 2 in a Van 't Hoff diagram. The state point of the water heat exchanger (blue circle) is always on the vapor pressure line of pure water, whereas the solution heat exchanger (green circle) changes between the isosteres of the rich (discharged) and poor (charged) solutions.

In [43], mechanical charging and discharging are described as follows (direct citation):

1. Discharging (Figure 2, left): The water heat exchanger works as evaporator, the sorption heat exchanger works as absorber. The evaporator has a slightly lower temperature than the absorber to enable the heat transfer. Water vapor from the evaporator is passed through an expansion machine to produce mechanical work W . The expanded water vapor is absorbed by the LiBr-solution in the absorber and the heat of absorption Q_{Abs} is used to evaporate more water. This goes on until the LiBr-solution is so diluted that the vapor pressure difference is not sufficient anymore to supply the desired mechanical power or torque. As the energy released when the water is absorbed is higher than the energy required for evaporation of that water (for the common physisorptive systems the ratio is around 1.1 . . . 1.2) the entire system heats up during discharge.
2. Charging (Figure 2, right): The sorption heat exchanger works as desorber. The LiBr-solution is regenerated by the input of heat from the water heat exchanger working

as condenser Q^{Cond} . The desorbed water vapor is compressed to condenser pressure level and liquefied in the condenser.

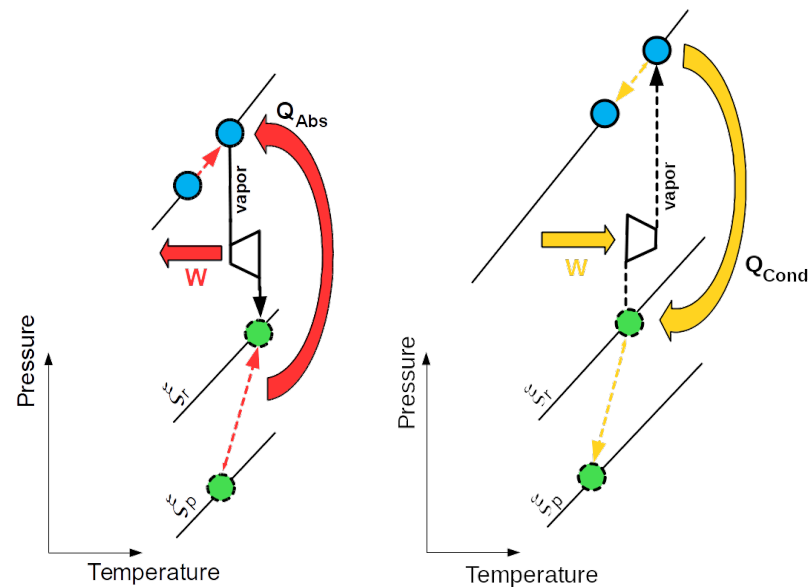


Figure 2. Mechanical discharging phase (left) and mechanical charging phase (right) [43].

2.2. Realization of the Heat Coupling

The coupling of the absorber/desorber (AD) with the evaporator/condenser (EC) can be realized in different ways:

- (A) Directly coupled (Figure 3): One heat exchanger (HX) is submerged in the other (this corresponds to the original design of Honigmann's fireless locomotive, as can be seen in [1]). This certainly minimizes the temperature differences for heat exchange and thus exergy destruction, but it also reduces the control possibilities and is a design challenge, especially as both HXs would have to be separated again for thermal charging.

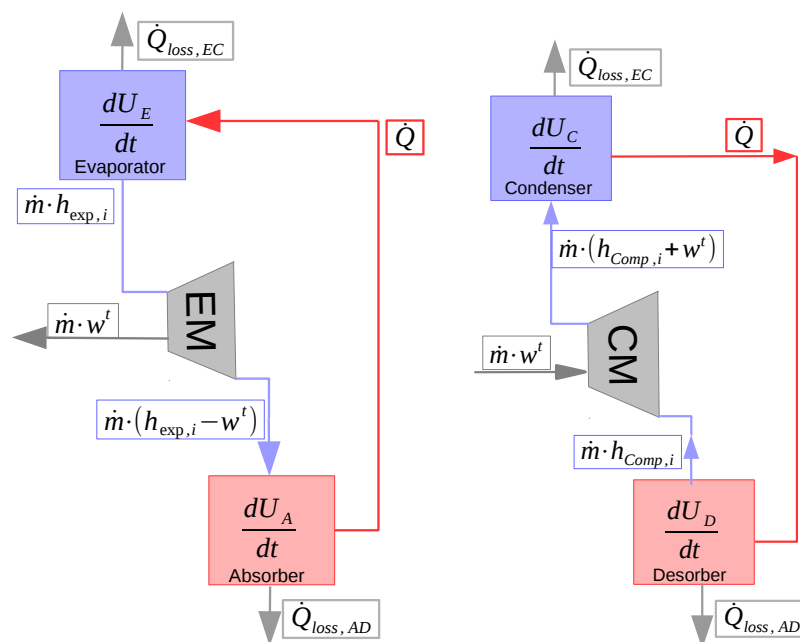


Figure 3. System configuration (A): Directly coupled HXs—mechanical discharging (left), mechanical charging (right).

(B) Coupled via an external heat-transfer circuit (Figure 4): Pipes with a heat-transfer fluid are connected the HXs. For thermal charging and control and, potentially, efficiency increase, external heat sink and source are integrated in the transfer circuit. This corresponds to the realization of the prototype plant at TU Berlin.

Furthermore, system configuration (C) is proposed (Figure 5) with the expansion machine (EM) being heated by the external heat-transfer circuit during the discharging process and the compression machine (CM) being cooled during the charging process ($\dot{Q}_M$). The equations for the thermal operation map are developed for all three configurations. The results are presented exemplarily for configuration A.

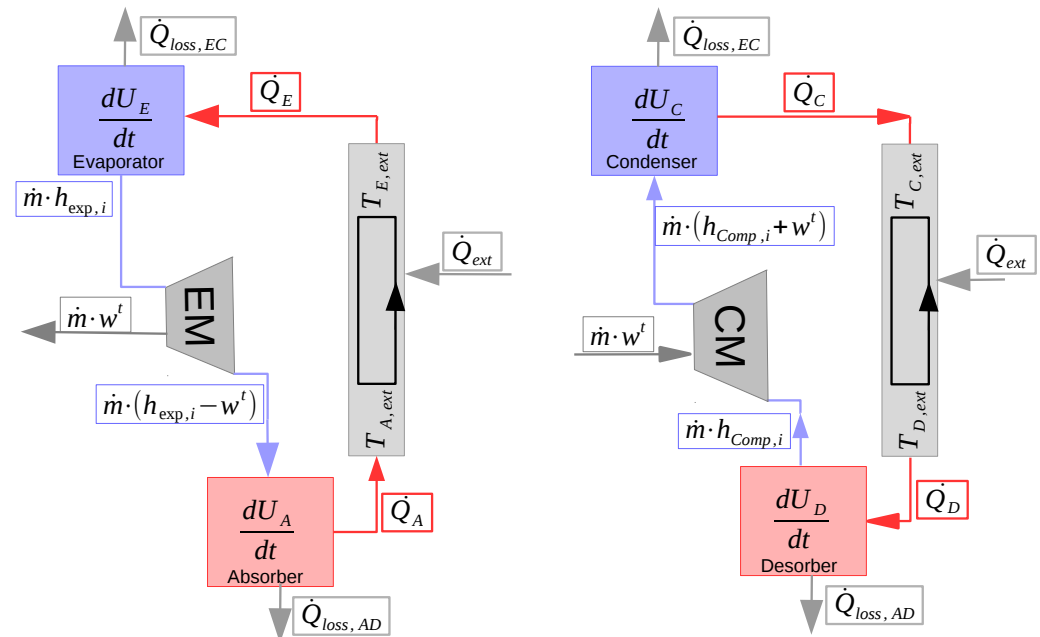


Figure 4. System configuration (B): Indirectly coupled HXs—mechanical discharging (left), mechanical charging (right).

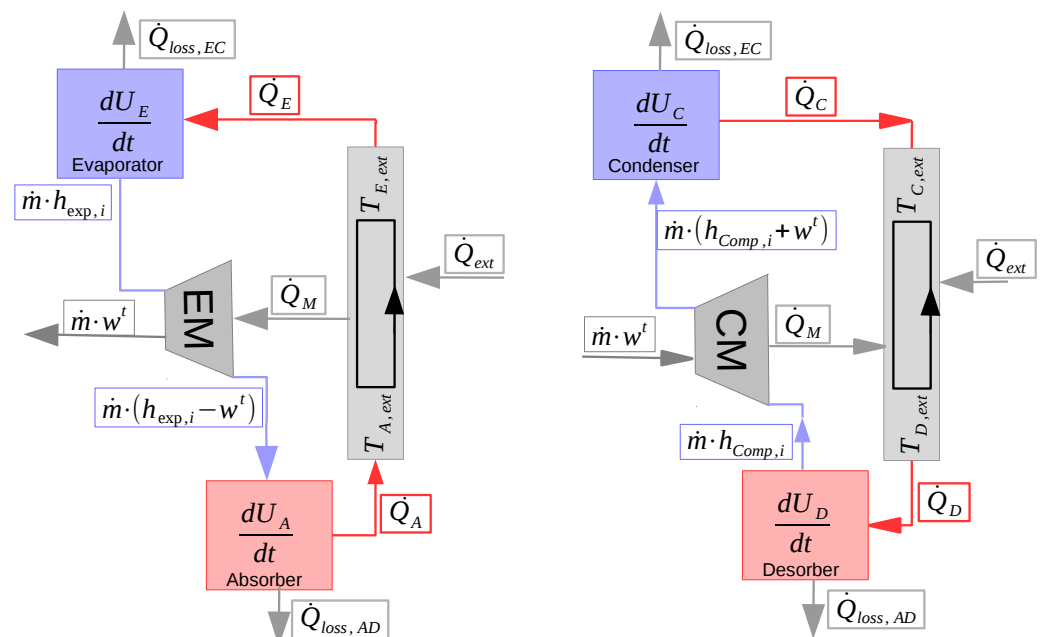


Figure 5. System configuration (C): Indirectly coupled HXs and heated/cooled expansion/compression machine—mechanical discharging (left), mechanical charging (right).

2.3. Solution-Field Geometry

The usable pressure potential during discharging depends on the salt mass fraction and temperature in the absorber (storage temperature T_S) and can be calculated using equilibrium property data of the working-fluid pair. The driving temperature difference for the heat transfer, $\Delta T_{dis} = T_S - T_E$, reduces this pressure potential (and thus the useful enthalpy difference). Analogously, during mechanical charging, the driving temperature difference, $\Delta T_{ch} = T_C - T_S$, raises the required enthalpy difference for vapor compression. This effect is illustrated in a schematic Van 't Hoff diagram in Figure 6. In Figure 7, the real Van 't Hoff diagram for aqueous LiBr is shown for a quantitative impression.

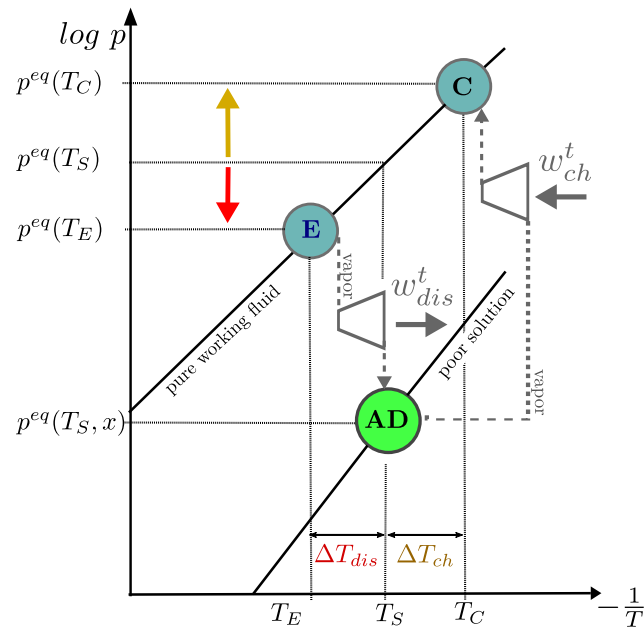


Figure 6. Influence of driving temperatures on usable/required pressure ratio in a Van 't Hoff diagram.

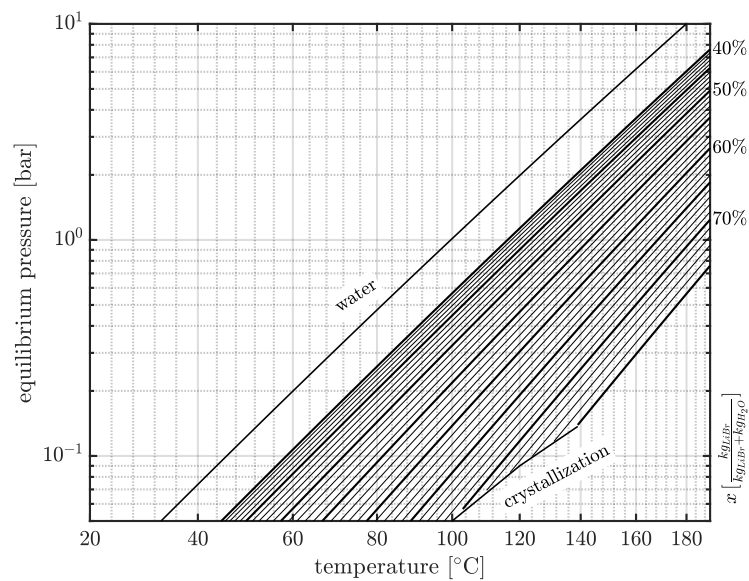


Figure 7. Van 't Hoff diagram for aqueous LiBr—property data taken from [45].

In Figure 8 (top), the useful (discharging) isentropic enthalpy differences, Δh_{isen} , of the water vapor are drawn over driving temperature difference ΔT (left) and working-fluid

mass fraction $\xi = 1 - x$ (right) for a storage temperature of $T_S = 130^\circ\text{C}$ (temperature of the absorber/desorber); the required (charging) enthalpy differences are shown, respectively, at the bottom of the figure. They are defined as:

$$\Delta h_{isen,dis} = h''(T_E) - h(s''(T_E), p^{eq}(T_S, x)) \quad (1)$$

$$\Delta h_{isen,ch} = h(s(p^{eq}(T_S, x), T_S), p^{eq}(T_C)) - h(p^{eq}(T_S, x), T_S) \quad (2)$$

Obviously, the isentropic enthalpy difference depends linearly on the driving temperature difference, ΔT . As the value of ΔT is actually specific to the HX design and process operation and is not a working-fluid-specific nor process-inherent property, its influence on the usable or required isentropic enthalpy difference is expressed by a thermal efficiency:

$$\eta_{th,dis} := \frac{\Delta h_{isen,dis}(\Delta T_{dis}, x, T_S)}{w_{rev,exp}^t(T_S, x)} \quad (3)$$

$$\eta_{th,ch} := \frac{w_{rev,compr}^t(T_S, x)}{\Delta h_{isen,ch}(\Delta T_{ch}, x, T_S)} \quad (4)$$

where the reversible shaft work $w_{rev}^t(T_S, x)$ equals the isentropic enthalpy difference if $\Delta T = 0$ (infinite HX area). Considering the linearity of the relation between Δh_{isen} and ΔT observed in Figure 8, the thermal efficiencies can be fitted according to Equations (5) and (6) with the proportionality factor $\Theta(T_S, x)$ in unit K^{-1} , which depends on storage temperature and salt mass fraction:

$$\eta_{th,dis} = 1 - \Theta_{dis} \Delta T_{dis} \quad (5)$$

$$\eta_{th,ch} = \frac{1}{1 + \Theta_{ch} \Delta T_{ch}} \quad (6)$$

A 3D fit of the proportionality factors $\Theta_{dis/ch} = f(T_S, x)$ is shown in Figure 9 on the right. The symbols represent the calculated values for $\Theta_{dis/ch}$ at driving temperatures $\Delta T = 1 \dots 10 \text{ K}$ for $T_S = 80 \dots 140^\circ\text{C}$ and $x = 0.5 \dots 0.7 \text{ kg salt/kg sol.}$ and represent the database for the shown polynomial fits. The corresponding fit functions are:

$$\begin{aligned} \Theta_{dis}(T_S, x) = & \left[2.42 - 1.62 \cdot \frac{(1-x)}{x_N} - 1.31 \cdot \frac{T_S}{T_{S,N}} + 8.89 \cdot \left(\frac{(1-x)}{x_N} \right)^2 \right. \\ & \left. - 8.52 \cdot \frac{(1-x)}{x_N} \cdot \frac{T_S}{T_{S,N}} + 2.91 \cdot \left(\frac{T_S}{T_{S,N}} \right)^2 \right] \% \end{aligned} \quad (7)$$

$$\begin{aligned} \Theta_{ch}(T_S, x) = & \left[6.15 - 1.50 \cdot \frac{(1-x)}{x_N} - 7.57 \cdot \frac{T_S}{T_{S,N}} + 8.75 \cdot \left(\frac{(1-x)}{x_N} \right)^2 \right. \\ & \left. - 8.48 \cdot \frac{(1-x)}{x_N} \cdot \frac{T_S}{T_{S,N}} + 5.72 \cdot \left(\frac{T_S}{T_{S,N}} \right)^2 \right] \% \end{aligned} \quad (8)$$

where the normalization factors are $x_N = 0.5 \text{ kg salt/kg sol.}$ and $T_{S,N} = 413.15 \text{ K}$.

On the left side of Figure 9, the thermal efficiencies for discharging (top) and charging (bottom) are shown in dependence of the corresponding driving temperature difference for different working-fluid mass fractions and in the middle of Figure 9 for different storage temperatures. The symbols represent the values calculated from enthalpy data. The lines are the corresponding functions of η_{th} (Equations (5) and (6), respectively) with the fitted proportionality factors Θ (Equations (7) and (8), respectively). Obviously, the match of fitted and calculated data is accurate.

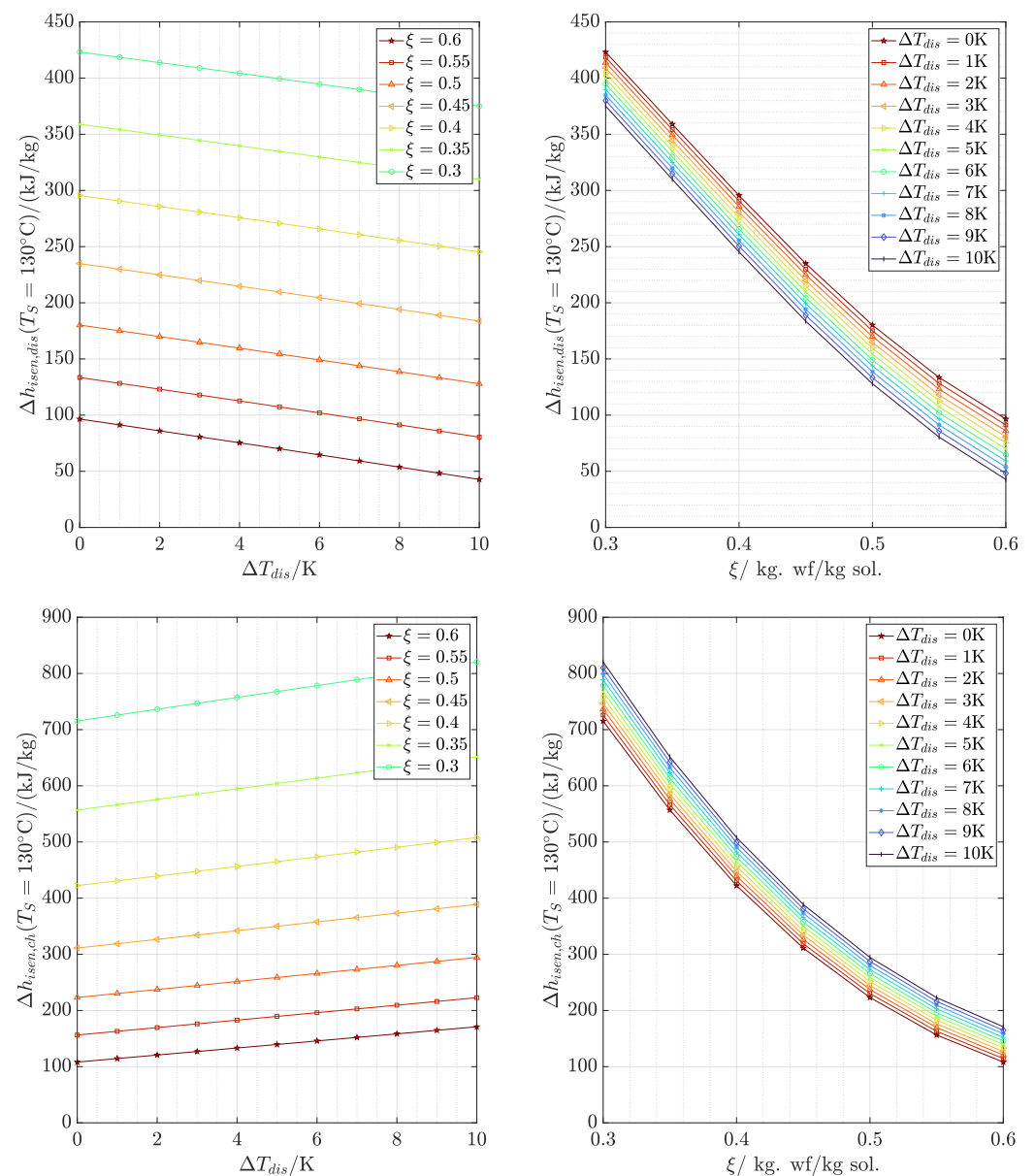


Figure 8. Isentropic enthalpy difference Δh_{isen} over working-fluid mass fraction and driving temperature difference for discharging (**top**) and charging (**bottom**).

Figure 9 also shows that the thermal efficiency is less sensitive to a raise in driving temperature difference during charging than during discharging; e.g., for a storage temperature of 130°C and a salt mass fraction of $0.5\text{ kg salt/kg sol.}$, the thermal efficiency for discharging drops by about $3\%/K$ of temperature difference, whereas for charging, it drops by around 2.8% at the 1st K and by around 2.4% at the 10th K.

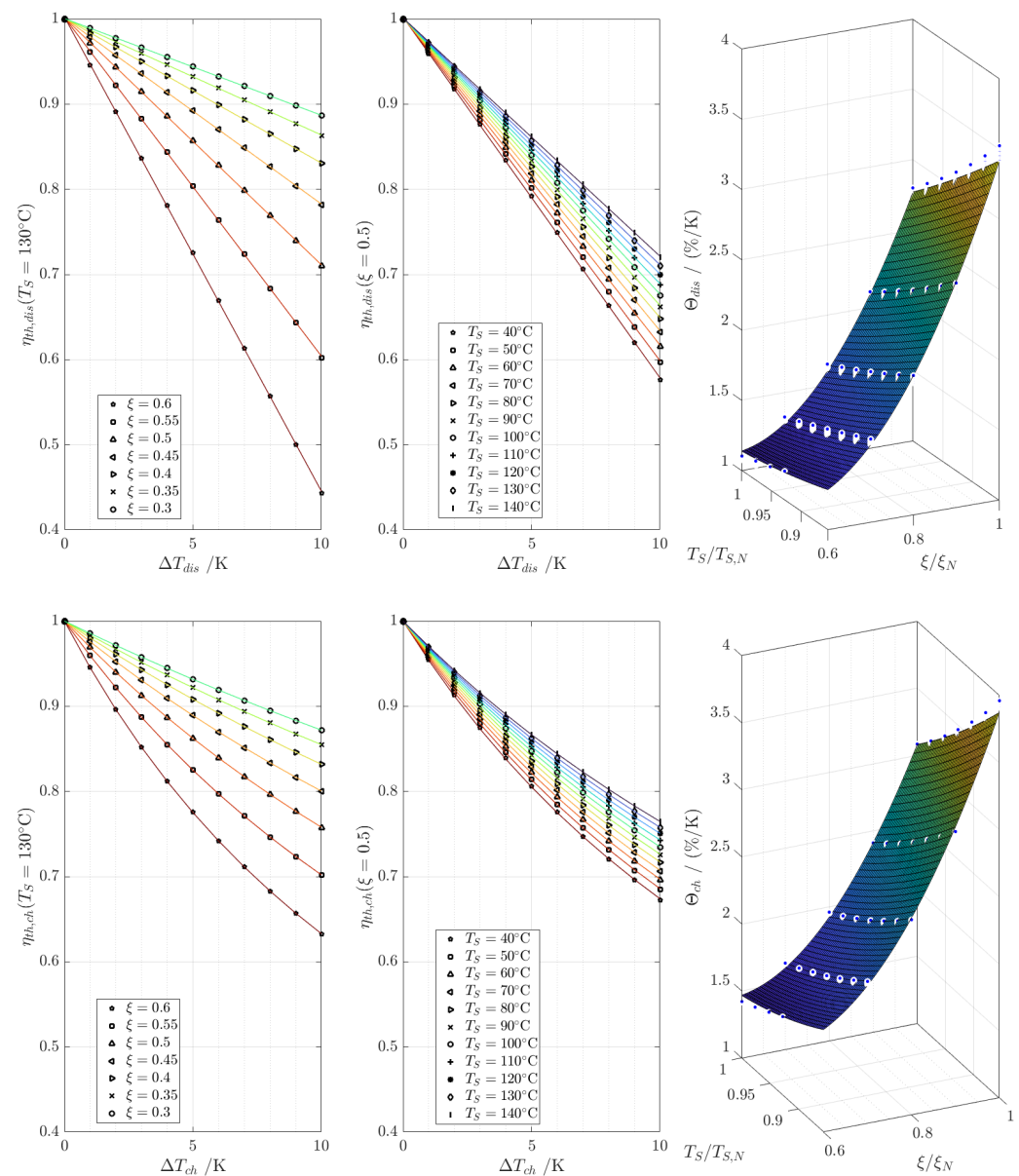


Figure 9. Thermal efficiency η_{th} and calculated proportionality factor $\Theta_{dis/ch}$ (Equations (7) and (8)) in dependence of storage temperatures and working-fluid mass fraction for discharging (**top**) and charging (**bottom**).

2.4. Guiding Differential Equations of the Charging and Discharging Process

The instationary energy balances for the heat exchangers and the stationary balances for the expansion/compression device and for the heat-transfer circuit are made under the following assumptions:

- The working fluids in the heat exchangers are in thermodynamic equilibrium;
- No vapor phase is present within the heat exchangers (the vapor is immediately absorbed by the liquid in A/condensed in C and immediately leaves D/E);
- The liquids in the heat exchangers are ideally mixed (retention time in the solution circuit is neglected; temperature is distributed equally); static pressure differences are negligible;
- The liquids are ideal, and $du = dh$ holds true;
- Heat and pressure losses in the connecting pipes are negligible (heat losses in the heat exchangers are considered);

- The component itself is at the same temperature as the respective working fluid contained.

For system configuration (A), this leads to the relations presented on the following landscape page. Inserting Equations (10) and (13) into Equations (9) and (12), respectively, a differential relation between the driving temperature difference for the heat exchange and the mass flow rate that is exchanged between E and A (discharging) or D and C (charging) is found.

For system configurations (B) and (C) of the heat coupling (defined in Section 2.2), similar differential equations are deduced, having the same structure. The corresponding parameters a, b, c and d of variable coefficients $f(t)$ and $g(t)$ are shown in Table 1. The underlying equations for all the cases can be found in Appendixes A and B.

Table 1. Variable coefficients of differential Equation (9).

Discharging	
a	$(c_{p,E} - \Theta \cdot w_{rev,exp}^t \cdot \eta_{vol} \cdot \eta_{i,EM}) \frac{1}{C_A}$
b	$\left(\frac{1}{C_A} + \frac{1}{C_E}\right)kA$, whereas $kA = \frac{k_{EA}k_{AA}}{k_{EA}k_{EA} + k_{AA}k_{AA}}$ for case B and C
c	$\frac{l_A - w_{rev,exp}^t \cdot \eta_{vol} \cdot \eta_{i,EM}}{C_A} + \chi \Delta h_E^{lv} \left(\frac{1}{C_E} + \frac{1}{C_A}\right)$
d	$\frac{\dot{Q}_{loss,E}}{C_E} - \frac{\dot{Q}_{loss,A}}{C_A} - kA \left(\left(\frac{1}{C_A} + \frac{1}{C_E}\right) \frac{1}{2\dot{C}_{htf}} - \frac{1}{C_A k_{EA} k_{EA}} + \frac{1}{C_E k_{AA} k_{AA}} \right) \dot{Q}_{ext} - kA \left(\left(\frac{1}{C_A} + \frac{1}{C_E}\right) \frac{1}{2\dot{C}_{htf}} + \frac{1}{C_A k_{EA} k_{EA}} - \frac{1}{C_E k_{AA} k_{AA}} \right) \dot{Q}_M$ =0, for case A =0, for case A and B
Charging	
a	$(\Delta c_{p,C}^{lv} + \Theta_{ch} \frac{w_{rev,comp}^t}{\eta_{vol,CM} \cdot \eta_{i,CM}}) \frac{1}{C_D} + \Theta_{ch} \frac{w_{rev,comp}^t}{\eta_{poly,CM}} \left(\frac{1}{C_D} + \frac{1}{C_C}\right)$
b	$\left(\frac{1}{C_D} + \frac{1}{C_C}\right)kA$, whereas $kA = \frac{k_{CA}k_{CD}k_{AD}}{k_{CA}k_{CA} + k_{CD}k_{AD}}$ for case B and C
c	$(l_A - \frac{w_{rev,comp}^t}{\eta_{vol,CM} \cdot \eta_{i,CM}}) \frac{1}{C_D} + (\Delta h_D^{lv} + \frac{w_{rev,comp}^t}{\eta_{poly,CM}}) \left(\frac{1}{C_C} + \frac{1}{C_D}\right)$
d	$\frac{\dot{Q}_{loss,C}}{C_C} - \frac{\dot{Q}_{loss,D}}{C_D} + kA \left(\left(\frac{1}{C_D} + \frac{1}{C_C}\right) \frac{1}{2\dot{C}_{htf}} - \frac{1}{C_D k_{CA} k_{CA}} + \frac{1}{C_C k_{AD} k_{AD}} \right) \dot{Q}_{ext} - kA \left(\left(\frac{1}{C_D} + \frac{1}{C_C}\right) \frac{1}{2\dot{C}_{htf}} + \frac{1}{C_D k_{CA} k_{CA}} - \frac{1}{C_C k_{AD} k_{AD}} \right) \dot{Q}_M$ =0, for case A =0, for case A and B

Discharging

$$\frac{d\Delta T_{dis}(t)}{dt} = - \left(\frac{1}{C_A} + \frac{1}{C_E} \right) kA \cdot \Delta T_{dis}(t) + \left(\chi \Delta h_E^{lv} \left(\frac{1}{C_A} + \frac{1}{C_E} \right) + \frac{l_A}{C_A} \right) \dot{m}(t) - \frac{P_{dis}^t(t)}{C_A} - \frac{c_{p,E}}{C_A} \Delta T_{dis}(t) \cdot \dot{m}(t) + \frac{\dot{Q}_{loss,E}}{C_E} - \frac{\dot{Q}_{loss,A}}{C_A} \quad (9)$$

$$P_{dis}^t(t) = \dot{m}(t) \cdot \eta_{vol,EM} \cdot w_{dis}^t = \dot{m}(t) \cdot \eta_{vol,EM} \cdot w_{rev,exp}^t(x(t), T_A) \cdot \eta_{i,EM} \cdot \eta_{th,dis}(x(t), T_A, \Delta T_{dis}(t)) \quad (10)$$

See Appendix A.3.1 for definition of efficiencies.

$$\begin{aligned} \frac{d\Delta T_{dis}(t)}{dt} = & - \underbrace{\left[(c_{p,E} - \Theta w_{rev,exp}^t \eta_{vol,EM} \eta_{i,EM}) \frac{1}{C_A} \dot{m}(t) + \left(\frac{1}{C_A} + \frac{1}{C_E} \right) kA \right]}_{f(t) := a\dot{m}(t) + b} \Delta T_{dis}(t) \\ & + \underbrace{\left(\left(l_A - w_{rev,exp}^t \eta_{vol,EM} \eta_{i,EM} \right) \frac{1}{C_A} + \chi \Delta h_E^{lv} \left(\frac{1}{C_E} + \frac{1}{C_A} \right) \right) \dot{m}(t) + \frac{\dot{Q}_{loss,E}}{C_E} - \frac{\dot{Q}_{loss,A}}{C_A}}_{g(t) := c\dot{m}(t) + d} \end{aligned} \quad (11)$$

Charging

$$\frac{d\Delta T_{ch}(t)}{dt} = - \left(\frac{1}{C_D} + \frac{1}{C_C} \right) kA \cdot \Delta T_{ch}(t) + \left((\Delta h_D^{lv} + w_{rev,comp}^t \eta_{isen,CM}) \left(\frac{1}{C_D} + \frac{1}{C_C} \right) + \frac{l_A}{C_D} \right) \dot{m}(t)$$

$$-\frac{P_{ch}^t(t)}{C_D} + \left(\Theta_{ch} w_{rev,comp}^t v_{isen,CM} \left(\frac{1}{C_D} + \frac{1}{C_C} \right) + \frac{\Delta c_{p,C}^{lv}}{C_D} \right) \Delta T_{ch}(t) \dot{m}(t) - \frac{\dot{Q}_{loss,C}}{C_C} + \frac{\dot{Q}_{loss,D}}{C_D} \quad (12)$$

$$P_{ch}^t(t) = \dot{m}(t) \frac{1}{\eta_{vol,CM}} w_{ch}^t = \dot{m}(t) \frac{1}{\eta_{vol,CM}} w_{rev,comp}^t(x(t), T_D) \frac{1}{\eta_{i,CM}} \frac{1}{\eta_{th,ch}(x(t), T_D, \Delta T_{ch}(t))} \quad (13)$$

See Appendix A.3.2 for definition of efficiencies.

$$\begin{aligned} \frac{d\Delta T_{ch}(t)}{dt} = & - \underbrace{\left[\left((\Delta c_{p,C}^{lv} + \Theta_{ch} \frac{w_{rev,comp}^t}{\eta_{vol,CM} \eta_{i,CM}}) \frac{1}{C_D} + \Theta_{ch} w_{rev,comp}^t v_{isen,CM} \left(\frac{1}{C_D} + \frac{1}{C_C} \right) \right) \dot{m}(t) + \left(\frac{1}{C_D} + \frac{1}{C_C} \right) kA \right] \Delta T_{ch}(t)}_{f(t) := a\dot{m}(t) + b} \\ & + \underbrace{\left((l_A - \frac{w_{rev,comp}^t}{\eta_{vol,CM} \eta_{i,CM}}) \frac{1}{C_D} + (\Delta h^{lv} + w_{rev,comp}^t v_{isen,CM}) \left(\frac{1}{C_C} + \frac{1}{C_D} \right) \right) \dot{m}(t) + \frac{\dot{Q}_{loss,C}}{C_C} - \frac{\dot{Q}_{loss,D}}{C_D}}_{g(t) := c\dot{m}(t) + d} \end{aligned} \quad (14)$$

Charge/Discharge time

In order to calculate the charge/discharge times, additionally, the following differential equation connecting the salt mass fraction and the mass flow rate is required:

$$\dot{m}(t) = \frac{dm_A}{dt} = \frac{d \frac{m_{salt}}{x}}{dt} = -m_{salt} \cdot \frac{1}{x^2} \frac{dx}{dt} \longrightarrow \dot{m}(t) dt = -m_{salt} \frac{1}{x^2} dx \quad (15)$$

Dimensionless representation

A dimensionless representation is used for an analysis of the system dynamic behavior in the following sections (Sections 3.1.1 and 3.1.2). The corresponding dimensionless variables and parameters are summarized in Table 2. The normalization factor for time t_N is defined over the working-fluid mass that is exchanged between A/D and E/C, so that t_N corresponds to the time it takes to charge/discharge 1% of the working-fluid mass at constant flow rate $\dot{m}_N$. The normalization factors for the driving temperature difference and mass flow rate are set to the nominal (design) values of the installation in question:

$$\frac{d\hat{\Delta T}_{dis/ch}(\hat{t})}{d\hat{t}} = (\hat{a} \cdot \hat{m}(\hat{t}) + \hat{b}) \cdot \Delta \hat{T}_{dis/ch}(\hat{t}) + \hat{c} \cdot \hat{m}(\hat{t}) + \hat{d} \quad (16)$$

$$\hat{m}(\hat{t}) d\hat{t} = - \frac{m_{salt}}{\dot{m}_N} \frac{1}{t_N} \frac{1}{x^2} dx = 100 \cdot \frac{x_{charged} \cdot x_{discharged}}{x^2} \frac{dx}{x_{charged} - x_{discharged}} \quad (17)$$

$$t_N = \frac{m_N}{\dot{m}_N} = \frac{0.01 \cdot \Delta m_{wf}}{\dot{m}_N} = 0.01 \cdot \frac{m_{salt}}{\dot{m}_N} \left(\frac{1}{x_{discharged}} - \frac{1}{x_{charged}} \right) \quad (18)$$

Table 2. Dimensionless variables and parameters of differential Equation (16).

Dimensionless Variables	Dimensionless Parameters
$\hat{t} = \frac{t}{t_N}$	$\hat{a} = a \cdot 0.01 \cdot \Delta m_{wf}$
$\Delta \hat{T}_{dis/ch}(\hat{t}) = \frac{\Delta T_{dis/ch}(t) - \Delta T_{dis/ch,N}}{\Delta T_{dis/ch,N}}$	$\hat{b} = b \cdot t_N = b \cdot \frac{0.01 \cdot \Delta m_{wf}}{\dot{m}_N}$
$\hat{m}(\hat{t}) = \frac{\dot{m}(t) - \dot{m}_N}{\dot{m}_N}$	$\hat{c} = c \cdot \frac{0.01 \cdot \Delta m_{wf}}{\Delta T_{dis,N}}$
	$\hat{d} = d \cdot \frac{t_N}{\Delta T_{dis,N}} = d \cdot \frac{0.01 \cdot \Delta m_{wf}}{\dot{m}_N \cdot \Delta T_{dis/ch,N}}$

3. Results

3.1. Quasi-Stationary Behavior of the System

Inhomogeneous differential Equations (11) and (14) of first order with variable coefficients can be solved using the variation of constants. Their general dimensionless solution is:

$$\Delta \hat{T}_{dis/ch}(\hat{t}) = \Delta \hat{T}_{dis/ch,h}(\hat{t}) + \Delta \hat{T}_{dis/ch,p}(\hat{t}) \quad (19)$$

$$= e^{-\hat{F}(\hat{t})} \left(c_i + \int \hat{g}(\hat{t}) \cdot e^{\hat{F}(\hat{t})} d\hat{t} \right) \quad (20)$$

where c_i is the integration constant and $\hat{F}(\hat{t})$ is the primitive of $\hat{f}(\hat{t})$. It is shown that the system tends to a quasi-stationary state, that is, $\frac{d\Delta \hat{T}}{d\hat{t}} = 0$. The validity of a model based on this assumption is discussed by comparing it to its dynamic counterpart.

3.1.1. Analysis for a Constant Vapor Mass Flow

For a constant vapor mass flow $\dot{m}(\hat{t}) = \dot{m}_c$ and a constant salt mass fraction x , the coefficients of the differential equation are also constants ($\hat{f}(\hat{t}) = \hat{f}$; $\hat{g}(\hat{t}) = \hat{g}$), and the analytical solution is:

$$\Delta \hat{T}_{dis/ch}(\hat{t}) = (\Delta \hat{T}_{dis/ch,0} - \frac{\hat{g}}{\hat{f}}) \cdot e^{-\hat{f} \cdot \hat{t}} + \frac{\hat{g}}{\hat{f}} \quad (21)$$

It should be noted that the heat capacities of the working fluids $c_{p,E}$, $c_{p,A}$, enthalpy of dilution l_A and heat losses in the HXs are dependent on the absolute temperature, which might change during the charging or discharging process. However, for the working-fluid pair in question, the change in absolute temperature is small during discharging (e.g., compare simulations in [44]); therefore, its influence on the working-fluid properties and heat losses is negligible.

In fact, the salt mass fraction is not constant either. As soon as there is a vapor mass flow between evaporator and absorber, the salt mass fraction in the absorber and the water mass in the evaporator change, and so do C_A and C_E . The same holds true for reversible shaft work w_{rev}^t , which changes with the pressure ratio, and for heat of dilution l_A . That means that $\hat{a} = \hat{a}(x(\hat{t}))$, $\hat{b} = \hat{b}(x(\hat{t}))$, $\hat{c} = \hat{c}(x(\hat{t}))$ and $\hat{d} = \hat{d}(x(\hat{t}))$.

However, if the working-fluid reservoir is large enough compared to the vapor mass flow rate (corresponding to long discharge times), the change in the salt mass fraction in time is very small, and so is its contribution to the dynamic behavior, as can be seen in the analyzed example.

Equation (21) shows that the temperature difference increases or decreases exponentially towards the value of $\frac{\hat{g}}{\hat{f}}$, in the case $\hat{f} > 0$. The value $\frac{\hat{g}}{\hat{f}}$ can be interpreted as the ratio of heat rate used or produced within the components to the heat transferred between the components per K of temperature difference when the system is in its rest position, where $\frac{\Delta \hat{T}_{dis/ch}}{d\hat{t}} = 0$, and:

$$\Delta \hat{T}_{dis/ch} = \Delta \hat{T}_{dis/ch,R} = \frac{\hat{g}}{\hat{f}} = \frac{\hat{c} \cdot \hat{m}_c + \hat{d}}{\hat{a} \cdot \hat{m}_c + \hat{b}} \quad (22)$$

The condition $\hat{f} = \hat{a} \cdot \hat{m}_c + \hat{b} > 0$ is fulfilled if (the factors for the dimensionless representation can be canceled; compare Table 2):

$$a \cdot m_c > -b. \quad (23)$$

For discharging, this means (compare Equation (11)):

$$\Theta_{dis} \cdot w_{rev,exp}^t \cdot \eta_{vol,EM} \cdot \eta_{i,EM} < \frac{kA}{\dot{m}} \cdot \left(1 + \frac{C_A}{C_E} \right) + c_{p,E}. \quad (24)$$

For the working-fluid pair LiBr/water at the operating conditions investigated here, we can estimate that $\Theta_{dis} < 5 \text{ \%}/\text{K}$ (compare Figure 9) and that $w_{rev}^t < 500 \text{ kJ/kg}$ (compare Figure 8); therefore:

$$(\Theta_{dis} \cdot w_{rev,exp}^t \cdot \eta_{vol} \cdot \eta_{i,EM} < 2.5 \text{ kJ/kg}) < (c_{p,E} > 4 \text{ kJ/kg}).$$

That means that Equation (24) is fulfilled for all mass flow rates, even in the absence of internal heat transfer ($kA = 0$), and for a given mass flow rate, the quasi-stationary working point after Equation (22) is always reached in finite time.

However, if heat-transfer capability kA is too small, the driving temperature difference of the rest position, which corresponds to a given mass flow rate, might be, in fact, too large and never be reached before the entire available pressure potential is gone (and the storage is already discharged). In this case, the quasi-stationary solution is out of the physical boundaries of the modeled system.

Therefore, $\hat{f}$ should not only be positive, but, more specifically, the parameters $\hat{a}$ and $\hat{b}$ should be large in order to achieve sufficiently small values of $\Delta\hat{T}_R$ for a given mass flow rate on the one hand and to lower the time constant and achieve small values of $\Delta\hat{t}$ between two quasi-stationary working points on the other hand.

That means that a large heat-exchanger area, a large heat-transfer coefficient and a working fluid with large heat capacity and a small Θ_{dis} are not only favorable for large thermal efficiency but also for the quasi-stationary operation of the system. Actually, a small Θ_{dis} equals to a small reduction in pressure potential per K ΔT_{dis} , which requires a small inclination of the vapor pressure line (compare Figure 6). This demands, according to Clausius–Clapeyron’s equation, a small evaporation enthalpy. So, a large Stefan number of the working fluid is not only favorable for the round-trip efficiency as reported by the author in [43], but also for the quasi-stationary operation of the discharging process.

Obviously, larger mass flow rates also lower the time constants but have a negative effect on the thermal efficiency, as the required heat for evaporation and thus the corresponding driving temperature rise.

For charging, we find that $\hat{f} > 0$ is always true for any working-fluid pair (compare Equation (14)) and that Θ_{ch} raises $\hat{f}$, so it lowers the time constant $\frac{1}{\hat{f}}$ of the system (therefore, contrary to discharging, a working fluid with a steeper vapor pressure line is favorable for fast thermal response of the system).

In Figure 10, Equation (21) is plotted in colored dashed lines for the discharging process at different starting conditions of $\Delta\hat{T}_{dis}$. The underlying parameters are reflected in Table 3 and are taken from the pilot plant at TU Berlin (see [42]); only the thermal masses of the periphery ($C_{EP/AP} = 0$) and the heat losses to the environment ($\dot{Q}_{loss,EC/AD} = 0$) were here neglected for simplicity. The resulting dimensionless parameter values of $\hat{a}$, $\hat{b}$, $\hat{c}$ and $\hat{d}$ are also listed, for $\hat{t} = 0$ and $\hat{t} = 5$.

From Table 3, it can be seen that parameters $\hat{b}$ and $\hat{c}$ are both three orders of magnitude larger than $\hat{a}$. Therefore, for mass flow rates around the nominal value, $\dot{m}_c \approx \dot{m}_N$, they are dominant for the solution of $\Delta\hat{T}_{dis}(t)$; the smaller the mass flow rate gets, the more dominant $\hat{b}$ (representing the heat transfer characteristics of the internal heat exchange) is, and the larger it gets, the more dominant $\hat{c}$ (representing working-fluid and expansion-device characteristics - the term includes evaporation and dilution enthalpies, the reversible shaft work and the EM efficiencies), is.

In Figure 10, one color represents the results for one constant mass flow rate (values are shown in dashed blue lines on the right abscissa). The corresponding rest positions $\Delta\hat{T}_{dis,R}$ are plotted in solid black lines. Their change in time (due to the change in the salt mass fraction) is rather small; e.g., for the largest mass flow rate (double nominal value), the change in the corresponding $\Delta\hat{T}_{dis,R}$ is $< 5\%$ after the exchange of 5% of working-fluid mass. Furthermore, it can be seen that the rest position, for all starting conditions of $\Delta\hat{T}_{dis}$, is always reached within a time frame of $\hat{t} = 3$, even for double the nominal mass flow rate.

$\hat{t} = 3$ is the time required to evaporate 3% of the available water mass (for a full discharge) at nominal flow (which equals 3 min for this example).

Therefore, the quasi-stationary solution $\frac{\Delta\hat{T}_{dis}}{dt} = 0$ of the mathematical model is only accurate for specific start conditions but is always reached in a relatively short time for a wide range of start conditions.

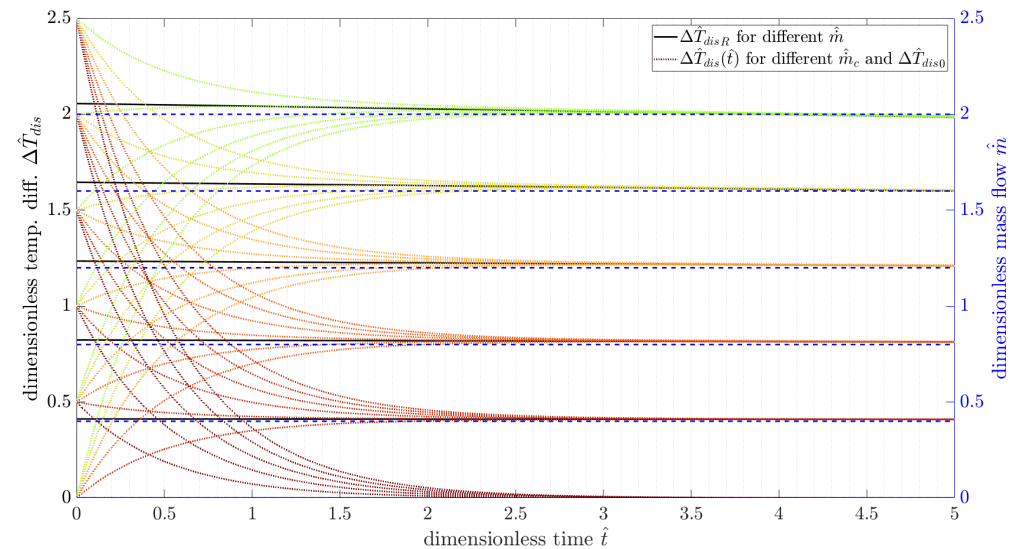


Figure 10. Dimensionless driving temperature difference over dimensionless time for different vapor mass flow rates $\hat{m}_{const}$ and different start values $\Delta\hat{T}_{dis0}$. Corresponding $\Delta\hat{T}_{disR}$ in solid black lines.

Table 3. Constant model parameters for the analyzed example.

Parameter	Value
heat-exchanger area A	1 m ²
heat-transfer coefficient k	1500 W/(K m ²)
inner efficiency of EM/CM $\eta_{EM/CM,i}$	0.8
heated expansion/cooled compression $\mu_{poly,EM/CM}$	1 (no)
volumetric efficiency of EM/CM $\eta_{vol,EM/CM}$	0.8
quality of produced water vapor χ	1
storage temperature T_{AD}	130 °C
mass of LiBr	30 kg
mass of water	60 kg
salt mass fraction, charged $x_{charged}$	0.7
salt mass fraction, discharged $x_{discharged}$	0.5
design mass flow rate $\dot{m}_N$	2.5 g/s
nominal time t_N for 1% discharged mass	68.57 s
design driving temperature difference $\Delta T_{dis,N}$	4 K
$\hat{a}(\hat{t} = 0/\hat{t} = 5)$	0.0026/0.0020
$\hat{b}(\hat{t} = 0/\hat{t} = 5)$	1.9250/1.6525
$\hat{c}(\hat{t} = 0/\hat{t} = 5)$	1.9900/1.6211
$\hat{d}(\hat{t} = 0/\hat{t} = 5)$	0/0

3.1.2. Analysis for a Linear Rising or Falling Vapor Mass Flow

The solution for constant mass flow rate is useful for a basic understanding of the system behavior but does not reflect realistic operation conditions at all. In order to control the storage power output, the mass flow rate has to be continuously adjusted. Therefore, the solutions of the differential equation are analyzed for mass flow rates changing linearly:

$$\dot{m}(\hat{t}) = \hat{\mu} \cdot \hat{t} + \hat{m}_0 \quad (25)$$

where the dimensionless change rate $\hat{\mu} = \mu \frac{t_N}{\dot{m}_N}$. For linearly changing mass flow rate, the variable coefficients of the differential equation are:

$$\hat{f}(\hat{t}) = \underbrace{\hat{a} \cdot \hat{\mu}}_{\alpha} \cdot \hat{t} + \underbrace{\hat{a} \cdot \hat{m}_0 + \hat{b}}_{\beta} \quad (26)$$

$$\hat{g}(\hat{t}) = \underbrace{\hat{c} \cdot \hat{\mu}}_{\gamma} \cdot \hat{t} + \underbrace{\hat{c} \cdot \hat{m}_0 + \hat{d}}_{\delta} \quad (27)$$

and the analytical solution is:

$$\Delta \hat{T}_{dis/ch}(\hat{t}) = e^{-(\frac{1}{2}\alpha \cdot \hat{t}^2 + \beta \cdot \hat{t})} \left[\Delta \hat{T}_{dis0} - \left(\underbrace{\frac{\delta}{\beta}}_{>0} - \underbrace{\frac{\gamma}{\beta^2}}_{sign(\mu)} \right) \right] + \left(\underbrace{\frac{\hat{g}(\hat{t})}{\hat{f}(\hat{t})}}_{>0} - \underbrace{\frac{\gamma}{\hat{f}(\hat{t})^2}}_{sign(\mu)} \right) \quad (28)$$

In Figure 11, Equation (28) is plotted in colored dashed lines for different start conditions of driving temperature difference and different linear functions of mass flow rates represented in different colors. The corresponding dimensionless mass flow rates are plotted in blue dashed lines on the right abscissa. The corresponding rest positions of the driving temperature difference are plotted in solid black lines. It can be seen that the quasi-stationary assumption $\frac{d\Delta T_{dis}}{dt} = 0$ leads to an underestimation of $\Delta \hat{T}_{dis}$ for a falling mass flow rate and to an overestimation for a rising mass flow rate. This is expressed in equations as follows:

$$\mu < 0 \rightarrow (\Delta \hat{T}_{dis\hat{t} \rightarrow \infty} - \Delta \hat{T}_{dis,R}) > 0 \quad (29)$$

$$\mu > 0 \rightarrow (\Delta \hat{T}_{dis\hat{t} \rightarrow \infty} - \Delta \hat{T}_{dis,R}) < 0 \quad (30)$$

That means that the thermal part of the system is slower than assumed by the quasi-stationary assumption and, in fact, requires more time to adapt to changing mass-flow-rate conditions.

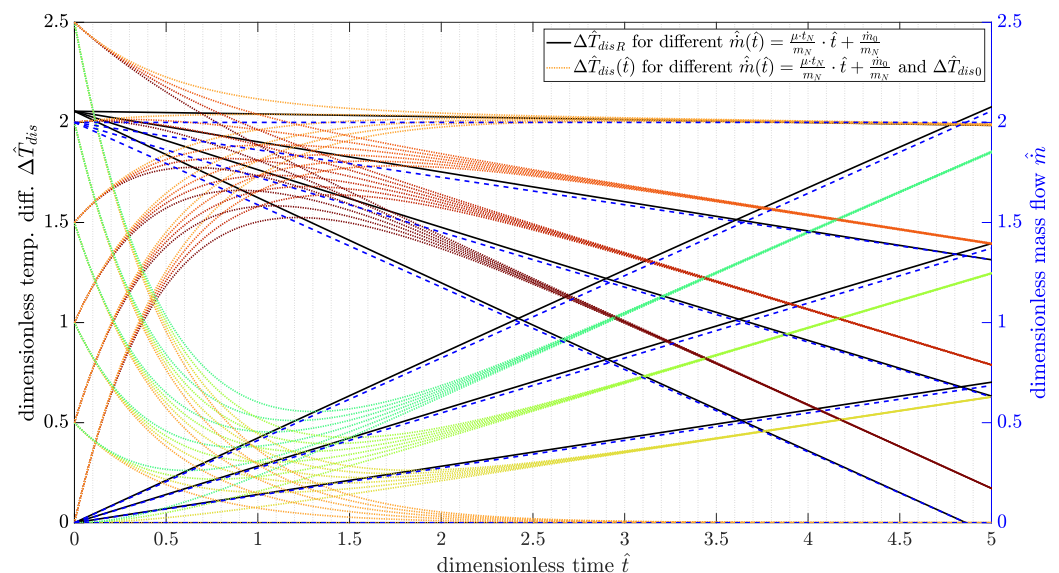


Figure 11. Non-dimensional driving temperature difference over non-dimensional time for different linearly rising and falling vapor mass flow rates $\hat{m}(\hat{t})$ and different start values $\Delta \hat{T}_{dis,0}$. Corresponding rest positions $\Delta \hat{T}_{dis,R}(\hat{t})$ in solid black lines.

It can also be stated that the larger the absolute change rate of mass flow rate $|\hat{\mu}|$ is, the larger the deviation of the rest position to the dynamic $\Delta \hat{T}_{dis}$ is. However, even for quite

a fast change rate, which corresponds to a dimensionless time smaller than 2.5 from 0 to design mass flow rate ($\hat{m} = 1$), the deviation of the corresponding rest position is $\approx 20\%$ at 100% nominal flow rate and $\approx 10\%$ when 200% nominal flow rate is reached.

Therefore, it can be concluded that the rest position ($\frac{d\hat{T}_{dis}}{d\hat{t}=0}$) can represent the storage's thermal operation conditions for sufficiently small change rates of mass flow rate for this specific example in an error band of $\leq 10\%$ for a change rate in mass flow from 0 to nominal in the dimensionless time of $\hat{t} = 2.5$ (corresponding to 2.5% of water mass evaporated in the evaporator).

3.2. Thermal Operation Maps

In the quasi-stationary state, for a certain mass flow rate through the system, there is a corresponding unique driving temperature difference for the heat exchange and vice versa. Thus, knowing the solution-field geometry presented in Section 2.3, the mechanical power retrieved from the storage can be calculated in dependence of the vapor mass flow rate and salt mass fraction with respect to the exergy destruction that is introduced with the requirement of a driving force for the heat exchange between absorber and evaporator/condenser and desorber $\Delta T_{dis/ch}$ to provide the vapor mass flow. That is called the *thermal operation map* of the storage, here.

3.2.1. Thermal Operation Map for Mechanical Discharging

The mechanical power output of the system in its rest position is calculated using Equation (9) and by applying the quasi-stationary assumption. For a size-independent representation, the power output is rated by the heat exchanger area A :

$$\begin{aligned} \frac{P_{dis,R}^t}{A} = & - \left(1 + \frac{C_A(x)}{C_E(x)} \right) k \cdot \hat{T}_{dis,R} \cdot \Delta T_{dis,N} \\ & + \left(\chi \Delta h^{lv} \left(1 + \frac{C_A(x)}{C_E(x)} \right) + l_A(x) - c_{p,E} \Delta T_{dis,R} \right) \frac{\dot{m}}{A} \\ & + \frac{\dot{Q}_{loss,E} \frac{C_A(x)}{C_E(x)} - \dot{Q}_{loss,A}}{A} \end{aligned} \quad (31)$$

The driving temperature of the rest position is calculated according to Equation (22). The thermal masses of evaporator and absorber are divided by the salt mass of the storage, and the influence of the thermal mass of the periphery is neglected for simplicity (for the equations with the thermal mass of the periphery, see Appendix C). Then, the ratio of $C_{A/D}(x)$ and $C_{E/C}(x)$ can be written as (the equation is also valid for the charging process):

$$\frac{C_{A/D}(x)}{C_{E/C}(x)} = \frac{c_{p,A} \cdot m_{A/D}(x)}{c_{p,E/C} \cdot m_{E/C}(x)} = \frac{c_{p,A}}{c_{p,E/C}} \frac{1}{\frac{x}{x_{discharged}} - 1 - \frac{x}{x_{charged} + \delta x_{buffer,EC}} + \frac{x}{x_{charged}}} \quad (32)$$

$\delta x_{buffer,EC}$ is a term introduced to account for a safety margin for the mass of water in the E/C at the end of discharging to avoid a dry-out and is here set to $\delta x_{buffer,EC} = 0.01 \frac{\text{kg salt}}{\text{kg sol}}$ (e.g., for the example in Table 3, this corresponds to a buffer mass of $m_{buffer,EC} = 0.6 \text{ kg}$).

The equation shows that, when neglecting the periphery's thermal mass, the derived thermal map is valid for all storage sizes (in terms of capacity), as only the salt mass fractions are required for calculating the ratios of $C_{A/D}(x)$ and $C_{E/C}(x)$.

The storage discharge time is calculated by integrating the differential equation connecting the salt mass fraction and the mass flow rate (Equation (15)). If the system is in its rest position, the mass flow rate only depends on the demanded power and salt mass fraction, not on time, so that the variables can be separated:

$$\int dt = -m_{salt} \int \frac{1}{x^2} \frac{1}{\dot{m}(x)} dx \quad (33)$$

For a discharge with constant mass flow, the integral can be solved analytically, so the time (multiplied by the HX area and per salt mass) for discharging to a salt mass fraction of x is:

$$\Delta t_{dis} \frac{A}{m_{salt}} = \frac{1}{\dot{m}_c} \cdot \left(\frac{1}{x} - \frac{1}{x_{charged}} \right) \quad (34)$$

For a discharge with constant power output, the integral on the right side is solved numerically using the tangential–trapezoidal rule with 401 lattice points. The required mass flow for the given power output has to be calculated iteratively from the two-dimensional system of nonlinear Equations (22) and (31). This was performed in MATLAB by the fsolve function with a function tolerance of 1×10^{-3} .

Combining Equations (22), (31) and (32) and using the proposed solutions for Equation (33), a map, as shown in Figure 12, can be found for a certain storage temperature, here for $T_S = 130^\circ\text{C}$.

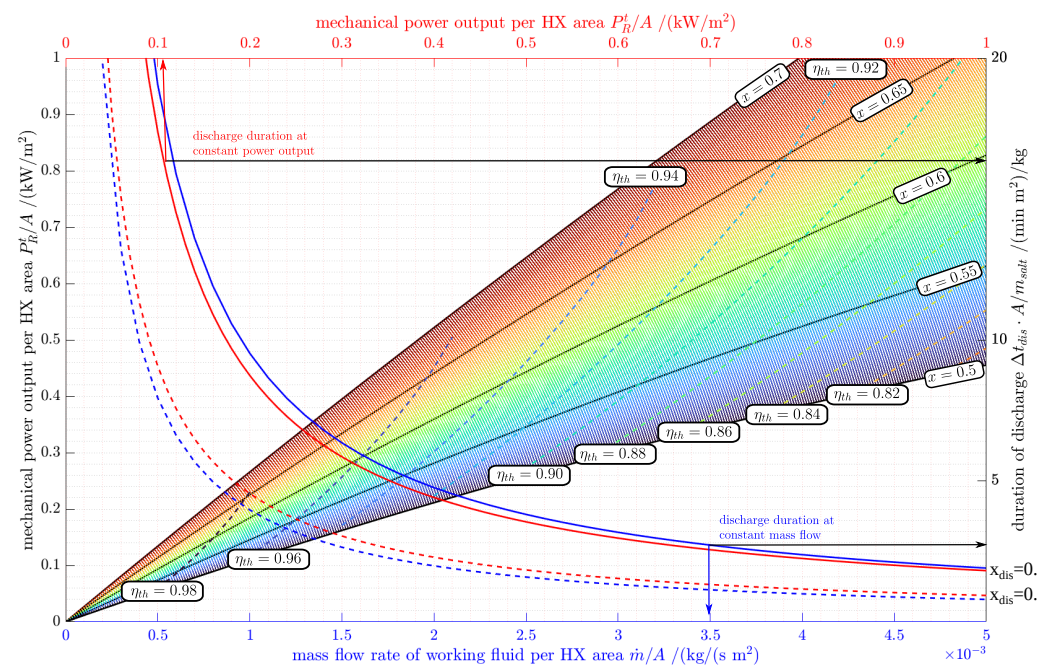


Figure 12. Operation map of the discharging process for the parameters reflected in Table 3.

One color of the rainbow corresponds to a certain salt mass fraction of the solution and thus to a certain state of charge of the storage. It shows the power output on the left abscissa over mass flow rate on the bottom ordinate for this specific state of charge. The larger the mass flow rate at a certain salt mass fraction is, the larger the mechanical power output is. Colored dashed lines of constant thermal efficiency η_{th} are additionally shown in the rainbow. The thermal efficiency rises with the salt mass fraction and declines with the mass flow rate.

The blue lines show the discharge time for different constant vapor mass flows (bottom ordinate), and the red lines show the discharge times for constant power outputs (top ordinate). The full lines represent a full discharge ($x = 0.7 - 0.5$) and the dashed lines, a half discharge ($x = 0.7 - 0.6$).

The map provided shows everything that is required to dimension an LAHMA storage with focus on the discharging of mechanical power for a specific application.

In Figure 13, a map is shown with the same parameters but reduced heat-transfer coefficient ($k = 1000 \text{ W/(K m}^2\text{)}$, compared with $k = 1500 \text{ W/(K m}^2\text{)}$ in Figure 12) and

with a semi-transparent layer behind with a map corresponding to a reduced storage temperature of $T_S = 80^\circ\text{C}$.

The influence of storage temperature on the specific power output is visible. It is due to the rise in thermal efficiency that is analyzed in Section 2.3.

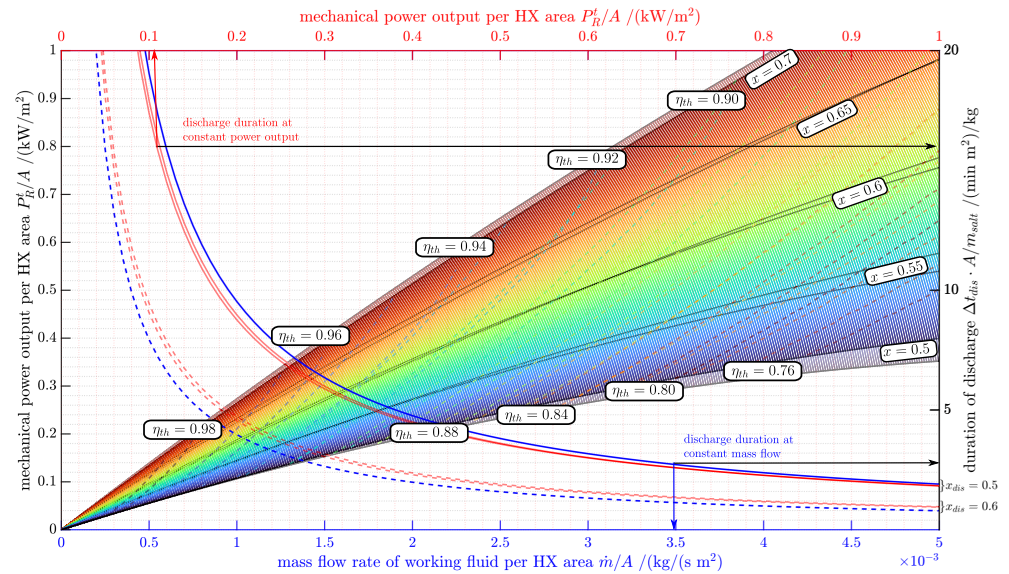


Figure 13. Operation map of the discharging process with the same parameters as in Table 3 but with $k = 1000 \text{ W/(K m}^2\text{)}$. Transparent in the background for comparison, the map is shown at the reduced storage temperature of $T_S = 80^\circ\text{C}$.

3.2.2. Thermal Operation Map for Mechanical Charging

For mechanical charging, if the system operates quasi-stationarily, the rated power output is:

$$\begin{aligned} \frac{P_{ch,R}^t}{A} = & - \left(1 + \frac{C_D(x)}{C_C(x)} \right) k \cdot \Delta \hat{T}_{ch,R} \cdot \Delta \hat{T}_{ch,N} \\ & + \left(\chi^{sh}(x) \Delta h^{lv} \left(1 + \frac{C_D(x)}{C_C(x)} \right) + l_A(x) - \Delta c_{p,C}^{lv} \Delta T_{ch,R} \right) \frac{\dot{m}}{A} \\ & + \frac{\dot{Q}_{loss,C} \frac{C_D(x)}{C_C(x)} - \dot{Q}_{loss,D}}{A} \end{aligned} \quad (35)$$

where (see Appendix A.1 for approximation of the amount of superheat):

$$\chi^{sh} := 1 + \frac{\Delta h^{sh}}{\Delta h^{lv}} \approx 1 + \frac{(1 + \Theta_{ch} \Delta T_{ch}) \cdot w_{rev,comp}^t(x) \cdot v_{isen,CM}}{\Delta h^{lv}} \quad (36)$$

The corresponding driving temperature difference $\Delta \hat{T}_{ch,R}$ is calculated using Equation (22) and the charging time for a constant mass flow rate as follows:

$$\Delta t_{ch} \frac{A}{m_{salt}} = \frac{1}{\frac{\dot{m}_c}{A}} \cdot \left(\frac{1}{x_{discharged}} - \frac{1}{x} \right) \quad (37)$$

Therefore, the thermal map in Figure 14 is found. Again, the colored dotted lines forming the rainbow show the power output (left abscissa) in dependence of the vapor mass flow rate (bottom ordinate) for different salt mass fractions (charging states of the storage system). The lines of the constant thermal efficiencies are dashed in the rainbow. The blue lines show the charge time (right abscissa) for different constant vapor mass flows (bottom ordinate), and the red lines show the discharge times for constant power outputs (top ordinate). The full lines represent a full charge and the dashed lines, a half discharge.

The provided map shows everything that is required to dimension an LAHMA storage with focus on the charging of mechanical power for a specific application.

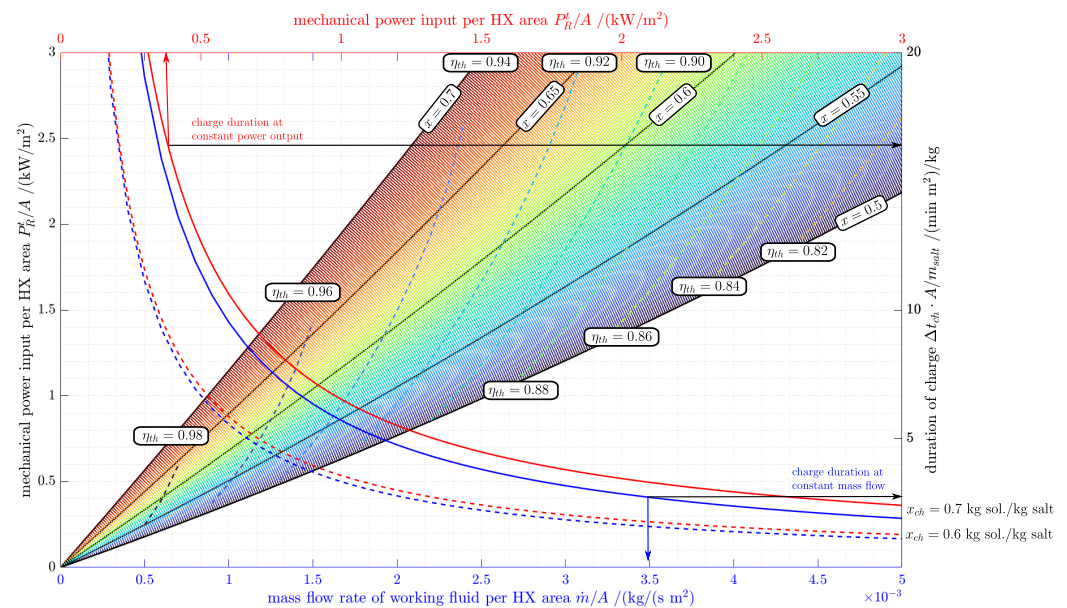


Figure 14. Operation map of the charging process for the parameters reflected in Table 3.

3.3. Further System Analyses

From the obtained set of equations, further system analyses can be conducted, e.g., the influence of cooled compression and heated expansion ($\dot{Q}_M > 0$), as mentioned for configuration (C), on the thermal efficiency, as defined in Section 2.3, of the system. It is clear that $\dot{Q}_M > 0$ can raise the inner machine efficiencies. As can be seen from parameter d in Table 1, it additionally reduces the quasi-stationary driving temperature difference (compare Equation (22)) under certain circumstances or raises it, under others, and raises or reduces thermal efficiencies η_{th} .

The smaller ΔT_{dis} for a certain mass flow rate is, the larger η_{th} is. The asymptotic value of $\Delta T_{dis/ch}$ for constant mass flow $\dot{m}_c$ is $\Delta T_{dis/ch,R} = \frac{g}{f} = \frac{c \cdot \dot{m}_c + d}{a \cdot \dot{m}_c + b}$. Therefore, the smaller g is, the larger η_{th} is. Now, d is reduced with $\dot{Q}_M$ if:

$$\left(\left(\frac{1}{C_{A/D}} + \frac{1}{C_{E/C}} \right) \frac{1}{2\dot{C}_{htf}} + \frac{1}{C_{A/D}k_{E/C}A_{E/C}} - \frac{1}{C_{E/C}k_{A/D}A_{A/D}} \right) > 0 \quad (38)$$

Thus, heated expansion/cooled compression as proposed in configuration (C) has a positive effect on thermal efficiency if:

$$NTU_{A/D} > \frac{1}{\frac{C_{E/C}(x)}{C_{A/D}(x)} \left(\frac{1}{2} + \frac{1}{NTU_E} \right) + \frac{1}{2}} \quad (39)$$

For the working-fluid pair LiBr/water at 130 °C, the value of $\frac{C_E(x)}{C_A(x)}$ ranges between ≈ 0 (fully discharged state: $x = 0.5 \frac{\text{kg salt}}{\text{kg sol}}$) and 1 (fully charged state: $x = 0.7 \frac{\text{kg salt}}{\text{kg sol}}$). Thus, it should be $NTU_{A/D} > \frac{NTU_E}{1+NTU_E}$ in the fully charged state and $NTU_{A/D} > 2$ in the fully discharged state. Therefore, whether heated expansion/cooled compression can raise thermal charging/discharging efficiency depends on the specific heat-transfer characteristics of the A/D unit compared to the E/C unit and on the ratio of thermal masses of both units, which is constantly changing during the process due to the transfer of working fluid from one to the other.

However, it should be noted that the equations for the configurations (B) and (C) are derived using the arithmetic mean temperature difference instead of a better approximation by the logarithmic mean for the heat exchange between the main heat exchangers A/D/E/C and the external heat-transfer circuit. This approximation is only valid for small NTUs ($\approx < 1$). For larger NTUs, as they are required in order to raise efficiency, the logarithmic driving temperature difference is smaller than its arithmetic pendant.

That means that, for a given mass flow rate, the driving temperature difference predicted by the set of derived equations is smaller than the one required in order to evaporate this mass flow rate. However, the effect of NTU values on parameter d should keep its direction even when using the logarithmic mean temperature difference or additional correction factors accounting for crossflow. The NTU value just needs to be even larger than that stated here.

Therefore, we can conclude that NTU_A should be much larger than 2 for a positive effect, during the entire discharging/charging process of expansion machine heating/compression machine cooling, not only on machine efficiency but also on the thermal efficiency of the entire process.

4. Discussion

4.1. Derived Storage Characteristics

Assuming a good agreement of the quasi-stationary model with reality (experimental validation is in progress), the mathematical analysis shows a very quick response time of the system towards its new rest position when disturbed. Obviously, the storage can deliver or consume a certain power very quickly, due to the fact that all the components of the entire system are at a similar temperature level at any time.

As already stated, this is an outstanding characteristic for a thermal-storage system that stores electrical energy. Common *Pumped Thermal Electricity Storage* systems are based, e.g., on Brayton, Joule, Clausius–Rankine or air-liquefaction cycles working at two distinguished temperature levels during charging/discharging.

The thermal map shows further storage characteristics quite clearly:

- The thermal efficiency of the process is very sensitive to the vapor mass flow rate;
- For discharging with constant thermal efficiency, the mass flow rate has to decline continuously;
- For charging with constant thermal efficiency, the mass flow rate has to rise continuously;
- The lower the mass flow rate is, the larger the thermal efficiency is—as usual, there is a trade-off between power and energy density/efficiency;
- For a constant power output during discharge, the mass flow rate has to rise during discharging (with the consequence of declining thermal efficiency);
- For a constant power input during charge, the mass flow rate has to decline during charging (with the consequence of rising thermal efficiency).

Comparing the two maps for the 80 and 130 °C storage temperatures in Figure 13, it can be seen that the thermal efficiency for discharging rises with smaller operating temperatures, as well as the mechanical power output. This is due to a slightly larger pressure ratio between the equilibrium pressures of water and aqueous LiBr for lower temperatures, as can be seen from the corresponding Van 't Hoff plot in Figure 7. It seems that lower temperatures are advantageous from this perspective, but they require larger expansion machines—especially for water vapor, the density drops significantly with temperature. Thus, lower temperatures might not be favorable when looking at storage cost and size.

Comparing the discharging and charging maps in Figures 12 and 14, it can be seen that:

- The mass flow rate for a certain power input is significantly smaller than for the same power output; in other words, if the power output and input are equal and fixed, charging takes more than 3 times longer than discharging in the range 0.5–1 kW/m²;

- The thermal efficiency for the same mass flow rate is always larger for discharging, because the heat of desorption is always larger than the heat of evaporation. Therefore, assuming similar overall heat-transfer coefficients for desorption/condensation and absorption/evaporation, the required temperature difference for a certain mass flow rate is larger when charging.

4.2. Critical Model Assumptions

The model is presented as generally as possible in order to make it universal, so certain effects which would occur in a real application are not modeled at all.

A critical assumption in the model is the ideal mixing within the HXs, especially in the AD. In the AD, the liquid solution has a changing density depending on the salt mass fraction. The liquid, being more dense (having a larger salt mass fraction), tends to occupy the ground level of the AD or associated liquid storage tanks. This would be the freshly desorbed liquid during charging (coming from the film desorber) or the liquid that has not yet absorbed vapor during discharging (flowing into the film absorber). The value of this modeling error depends on the realization of the AD and its connection with the liquid storage tanks.

Another critical assumption is that of thermodynamic equilibrium. The effects of superheating or subcooling in the liquid or gas phases occur in a real application. However, the amount depends on the realization of the heat-exchanger design, the working-fluid pair and heat-transfer fluid used and on the flow rates applied.

Furthermore, the parameters reflected in Table 3 are assumed to be constant. In reality, the expansion and compression machine efficiencies definitely change with the change in the pressure ratio and change in rotational speed (speed control would be required for controlling the power output). Again, the significance of variation depends on the machine that is used. Looking at the equations, the inner machine efficiencies have a large influence on the power output/input but a small influence on the quasi-stationary value of ΔT_R .

Depending on the chosen configuration, the working-fluid pair and the significance of heat losses, the storage temperature changes during the charging/discharging process. However, as the heat of dilution is in the same order of magnitude as the expansion/compression machine work, and the heat losses are insignificant, the temperature change is small and slow or might even be controlled by an external heat source/sink via $\dot{Q}_{ext}$ or internal heat management via $\dot{Q}_M$ (see system configuration (C)).

If the derived equations are applied for the configurations (B) and (C), one should be aware that the power output prediction would be overestimated and the input prediction, underestimated, respectively. This is due to the assumption of an arithmetic mean temperature difference instead of, e.g., a logarithmic one for the heat transfer at the A/D and E/C if an external heat-transfer circuit is present. However, the lower the corresponding NTU values of A/D and E/C are, the better the assumption fits to reality. Therefore, the larger the heat capacity flow in the heat-transfer circuit is, the better the prediction is (e.g., usually, for $NTU < 1$, the difference in arithmetic and logarithmic driving temperature difference is smaller than 10%).

5. Conclusions

The derived method makes it possible to easily assess the interdependency of mass flow rate and driving temperature difference; therefore, it allows one to predict storage behavior for arbitrary power in-/output and for arbitrary expansion/compression machine types.

The mathematical analysis shows that for a storage system, where absorber and evaporator are directly coupled (system configuration (A)) and where the model assumptions reflected in Section 3.1 are applicable, the mechanical discharging process can be reasonably assumed to be quasi-stationary (meaning that $\frac{d\Delta T_{dis}}{dt} = 0$) if the change in mass flow rate is rather small. Then, the derived thermal operation map is valid independently of the

starting conditions of the system, and the thermal map and the underlying equations can be used for general system analysis and optimization.

Some important storage characteristics were derived: First of all, the thermal-storage efficiency is very sensitive to the exchanged vapor mass flow rate. The round-trip efficiency of the system, therefore, depends on the specific charging and discharging scenario in terms of power. The larger the power density of the storage system is, the lower the thermal efficiency is.

Secondly, for a specific mass flow rate, the thermal efficiency for charging is always lower than that for discharging in the analyzed configuration (A). Generally, the round-trip efficiency for a full charge/discharge is low for this configuration. Measures to enhance the charging efficiency should be taken, e.g., diabatic compression.

More generally, internal and external heat management can be optimized with the help of the derived equations for configurations (B) and (C). In fact, heated expansion and cooled compression raise not only inner machine efficiencies but also thermal efficiency η_{th} of the entire discharging/charging process, if $NTU_{A/D} \gg 2$. It is worthwhile, therefore, to consider this configuration, as it would lead to a significant gain in overall storage efficiency. The quantitative analysis of the gain is work in progress.

Besides those thermal system analyses, the quasi-stationary model and the developed thermal operation maps for the storage's charging and discharging process help to:

- Dimension the storage components (heat exchanger, expansion/compression device, liquid storage tanks);
- Compare different liquid-sorption working-fluid pairs;
- Conduct economic analyses to find the optimal heat-exchanger size for different energy production scenarios (e.g., long or short-term reserves);
- Develop a model-based control strategy for the power output of the storage.

Furthermore, the quasi-stationary model is applicable to other working-fluid pairs with known equilibrium data. The system might be optimized with the help of the derived equations in terms of working fluid and working temperature.

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Nomenclature

χ	vapor quality
η	energetic efficiency
ΔT	driving temperature difference (K)
η	energetic efficiency
ν_{isen}	isentropic ratio
Θ	fitted parameter (%/K)
ξ	mass fraction ($\frac{\text{kg working fluid}}{\text{kg sorbant}}$)
a, b, c, d	parameters of the diff. eq.

A	heat-exchanger area (m^2)
c_p	isobaric heat capacity ($\frac{\text{kJ}}{\text{kg}}$)
Δc_p^{lv}	difference in liquid and gaseous isobaric heat capacity ($\frac{\text{kJ}}{\text{kg}}$)
d	differential operator
f	variable coeff. of the diff. eq. ($\frac{\text{K}^2}{\text{s}}$)
g	variable coeff. of the diff. eq. ($\frac{\text{K}}{\text{s}}$)
h	specific enthalpy ($\frac{\text{kJ}}{\text{kg}}$)
Δh_A	sorption enthalpy ($\frac{\text{kJ}}{\text{kg}}$)
Δh^{lv}	evaporation enthalpy ($\frac{\text{kJ}}{\text{kg}}$)
Δh^{sh}	superheat at compressor outlet ($\frac{\text{kJ}}{\text{kg}}$)
k	heat-transfer coefficient ($\frac{\text{W}}{\text{K m}^2}$)
m	mass (kg)
p	pressure (Pa)
P^t	shaft power (W)
R	universal gas constant ($\frac{\text{kJ}}{\text{kg K}}$)
s	specific entropy ($\frac{\text{kJ}}{\text{kg}}$)
t	time (s)
T	temperature (K)
q	specific heat ($\frac{\text{kJ}}{\text{kg}}$)
Q	heat (kJ)
U	inner energy (kJ)
v	specific volume ($\frac{\text{m}^3}{\text{kg}}$)
w^t	specific shaft work ($\frac{\text{kJ}}{\text{kg}}$)
x	salt mass fraction ($\frac{\text{kg salt}}{\text{kg sorbant}}$)

Abbreviations

A	ab-/adsorber
D	desorber
E	evaporator
EM	expansion machine
C	condenser
CB	Carnot battery
CM	compression machine
HX	heat exchanger
P	component parts/periphery
PTES	Pumped Thermal Electricity Storage
NTU	number of transfer units
sol.	solution

Indices

$\wedge$	dimensionless quantity
$'$	saturated liquid
$''$	saturated vapor
s	storage
A	ad-/absorbant
eq	equilibrium
ch	charge
dis	discharge
$comp$	compression
exp	expansion
rev	reversible limit
$isen$	isentropic
$poly$	polytropic
vol	volumetric
htf	heat-transfer fluid
i	inlet

o outlet
p particulate
h homogeneous

Appendix A. Energy Balances

Appendix A.1. Evaporator(E)/Condenser(C)

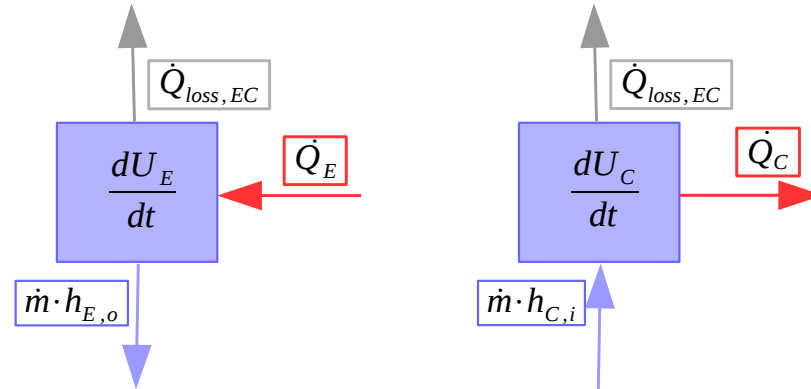


Figure A1. Energy balance of evaporator for discharging (**left**) and condenser for charging (**right**).

$$\frac{dU_E}{dt} = \dot{Q}_E - \dot{m} \cdot h_{E,o}(T_E, \chi) - \dot{Q}_{loss,E} \quad (A1)$$

$$\frac{dU_C}{dt} = -\dot{Q}_C + \dot{m} \cdot h_{C,i} - \dot{Q}_{loss,C} \quad (A2)$$

where χ is the vapor quality of the escaping mass flow.

The internal energy of the evaporator/condenser consists of the internal energy of the working fluid within the component and the internal energy of the component itself and connected periphery $dU_{E/C,P} = C_{E/C,P} dT_{E/C}$ (pipes, walls, etc.):

$$\frac{dU_{E/C}}{dt} = \frac{dm_{E/C}}{dt} \cdot h_{E/C}(T_{E/C}) + m_{E/C} \frac{dh_{E/C}(T_{E/C})}{dt} + C_{E/C,P} \frac{dT_{E/C}}{dt}, \quad (A3)$$

where $h_{E/C}$ is the enthalpy of the liquid working fluid in the E/C.

Inserted into Equations (A1) and (A2) and with $\dot{m} = -\frac{dm_E}{dt} = \frac{dm_C}{dt}$ and $dh_{E/C} = c_p dT_{E/C}$, we find for the heat flow into/out of the component:

$$\dot{Q}_E = \dot{m}(h_{E,o}(T_E, \chi) - h_E(T_E)) + \underbrace{(m_E \cdot c_{p_E} + C_{E,P})}_{C_E(x)} \frac{dT_E}{dt} + \dot{Q}_{loss,E} \quad (A4)$$

$$\dot{Q}_C = \dot{m}(h_{C,i} - h_C(T_C)) - \underbrace{(m_C \cdot c_{p_C} + C_{C,P})}_{C_C(x)} \frac{dT_C}{dt} - \dot{Q}_{loss,C} \quad (A5)$$

As the mass of working fluid in the E/C depends on the salt mass fraction in the A/D, the thermal masses C_E and C_C are a function of x .

With the definition of the vapor quality χ , the output enthalpy in Equation (A4) can be replaced by:

$$h_{E,o}(T_E, \chi) = \chi \cdot h''(T_E) + (1 - \chi) \cdot h'(T_E), \quad (A6)$$

and as $h_E = h'(T_E)$, we find:

$$\dot{Q}_E = \dot{m} \cdot \chi \Delta h^{lv} + C_E(x) \frac{dT_E}{dt} + \dot{Q}_{loss,E} \quad (A7)$$

where $h_{A/D}$ is the enthalpy of the liquid sorbate.

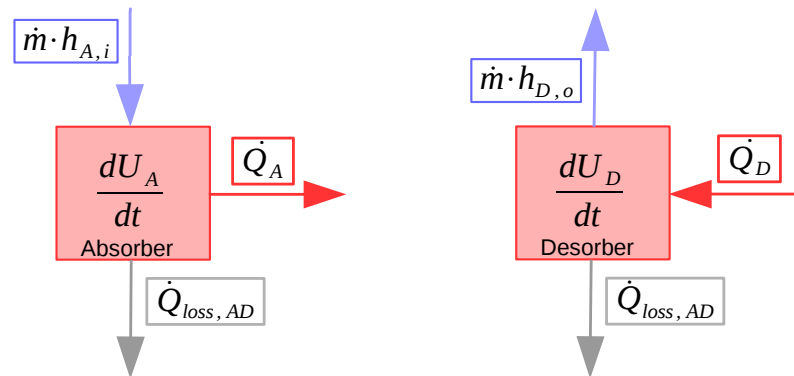


Figure A3. Energy balance of absorber for discharging (**left**) and desorber for charging (**right**).

Inserted into Equations (A12) and (A13) and with $\dot{m} = \frac{dm_A}{dt}$ for discharging and $\dot{m} = -\frac{dm_D}{dt}$ for charging, we find, for the heat flow into/out of the A/D:

$$\dot{Q}_A = \dot{m}(h_{A,i} - h_A(T_A, x)) - m_A \frac{dh_A(T_A, x)}{dt} - C_{AP} \frac{dT_A}{dt} - \dot{Q}_{loss,A} \quad (\text{A15})$$

$$\dot{Q}_D = \dot{m}(h_{D,o} - h_D(T_D, x)) + m_D \frac{dh_D(T_D, x)}{dt} + C_{DP} \frac{dT_D}{dt} + \dot{Q}_{loss,D} \quad (\text{A16})$$

The working fluid in the E or D has a lower temperature than the working fluid in the A or C. Between those two temperatures, the heat capacity can be set constant, so that:

$$h_{E/C}(T_{A/D}) - h_{E/C}(T_{E/C}) = c_{p_{E/C}}(T_{A/D} - T_{E/C}) \quad (\text{A17})$$

together with the definition of the solution enthalpy:

$$l(T_{A/D}, x) := \underbrace{h'(T_{A/D})}_{\text{sat. enthalpy of liquid water}} - \underbrace{h_{A/D}^{eq}(x, T_{A/D})}_{\text{equ. enthalpy of solution}} + x \underbrace{\frac{\partial h_{A/D}^{eq}(x, T_{A/D})}{\partial x}}_{\text{excess enthalpy}}, \quad (\text{A18})$$

and with $h'(T_{A/D}) = h_{E/C}(T_{A/D})$, the enthalpy differences in the brackets behind the mass flow rates in Equations (A15) and (A16) can be written as:

$$\begin{aligned} h_{A,i/D,o} - h_{A/D}(T_{A/D}, x) \\ = h_{A,i/D,o} - h_{E/C}(T_{E/C}) + h_{E/C}(T_{E/C}) - h_{A/D}(T_{A/D}, x) \end{aligned} \quad (\text{A19})$$

$$\begin{aligned} = h_{A,i/D,o} - h_{E/C}(T_{E/C}) + l(T_{A/D}, x) - x \frac{\partial h_{A/D}(T_{A/D}, x)}{\partial x} \\ - c_{p_{E/C}}(T_{A/D} - T_{E/C}) \end{aligned} \quad (\text{A20})$$

Using the differential for the enthalpy of the absorbate:

$$\frac{dh_{A/D}(T_{A/D}, x)}{dt} = \frac{\partial h_{A/D}(x, T_{A/D})}{\partial x} \frac{dx}{dt} + \frac{\partial h_{A/D}(x, T_{A/D})}{\partial T_{A/D}} \frac{dT_{A/D}}{dt} \quad (\text{A21})$$

$$= \frac{\partial h_{A/D}(x, T_{A/D})}{\partial x} \frac{dx}{dt} + c_{p_{A/D}}(x) \frac{dT_{A/D}}{dt} \quad (\text{A22})$$

Equations (A15) and (A16) can be written as:

$$\begin{aligned}\dot{Q}_A = & \dot{m} \left(h_{A,i} - h_E(T_E) + l(T_A, x) - x \frac{\partial h_A(T_A, x)}{\partial x} - c_{pE}(T_A - T_E) \right) \\ & - m_A \left(\frac{\partial h_A(x, T_A)}{\partial x} \frac{dx}{dt} + c_{pA}(x) \frac{dT_A}{dt} \right) - C_{AP} \frac{dT_A}{dt} - \dot{Q}_{loss,A}\end{aligned}\quad (A23)$$

$$\begin{aligned}\dot{Q}_D = & \dot{m} \left(h_{D,o} - h_C(T_C) + l(T_D, x) - x \frac{\partial h_D(T_D, x)}{\partial x} + c_{pC}(T_C - T_D) \right) \\ & + m_D \left(\frac{\partial h_D(x, T_D)}{\partial x} \frac{dx}{dt} + c_{pD}(x) \frac{dT_D}{dt} \right) + C_{DP} \frac{dT_D}{dt} + \dot{Q}_{loss,D}\end{aligned}\quad (A24)$$

whereas the terms with the partial differentials of the solution enthalpy can be canceled out, because (see also Equation (15)):

$$m_A \cdot dx = -x \cdot dm_A = -x \cdot \dot{m} \cdot dt. \quad (A25)$$

$$m_D \cdot dx = -x \cdot dm_D = x \cdot \dot{m} \cdot dt. \quad (A26)$$

It follows:

$$\begin{aligned}\dot{Q}_A = & \dot{m} (h_{A,i} - h_E(T_E) + l(x, T_A) - c_{pE} \Delta T_{dis}) \\ & - \underbrace{(m_A \cdot c_{pA}(x) + C_{AP})}_{C_A(x)} \frac{dT_A}{dt} - \dot{Q}_{loss,A}\end{aligned}\quad (A27)$$

$$\begin{aligned}\dot{Q}_D = & \dot{m} (h_{D,o} - h_C(T_C) + l(x, T_D) + c_{pC} \Delta T_{ch}) \\ & + \underbrace{(m_D \cdot c_{pD}(x) + C_{DP})}_{C_D(x)} \frac{dT_D}{dt} + \dot{Q}_{loss,D}\end{aligned}\quad (A28)$$

where $\Delta T_{dis} := T_A - T_E$ and $\Delta T_{ch} := T_C - T_D$.

Appendix A.3. Expansion-/Compression Machine (EM/CM)

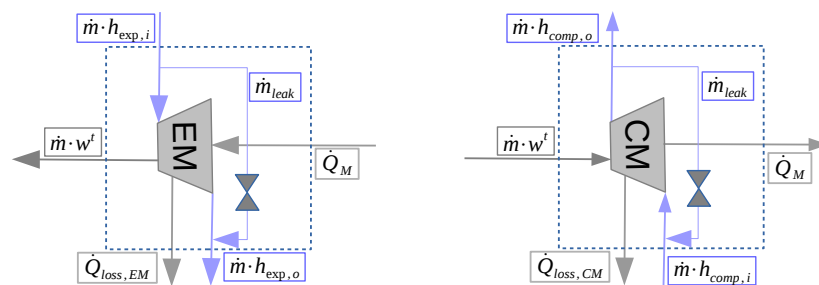


Figure A4. Energy balance of expansion device (left) and compression device (right).

$$\frac{dU_{EM}}{dt} = \dot{m}(h_{Exp,i} - w^t - h_{Exp,o}) + \dot{Q}_M - \dot{Q}_{loss,EM} \quad (A29)$$

$$\frac{dU_{CM}}{dt} = \dot{m}(h_{Comp,i} - h_{Comp,o} + w^t) - \dot{Q}_M - \dot{Q}_{loss,CM} \quad (A30)$$

The expansion/compression device is small compared with the large heat exchangers with working fluid and storage reservoir. For that reason and for simplicity, changes in the internal energy within the expansion device are neglected. w^t is not the measured mechanical work w_{mech}^t here, but:

$$w_{dis}^t = w_{rev,exp}^t \cdot \eta_{i,EM} \cdot \eta_{th} \quad (A31)$$

$$w_{ch}^t = w_{rev,comp}^t \cdot \frac{1}{\eta_{i,CM}} \cdot \frac{1}{\eta_{th}} \quad (A32)$$

For the enthalpy at the outlet, we find:

$$h_{Exp,o} = h_{Exp,i} - w^t + q_M - \frac{\dot{Q}_{loss,EM}}{\dot{m}} \quad (A33)$$

$$h_{Comp,o} = h_{Comp,i} + w^t - q_M - \frac{\dot{Q}_{loss,CM}}{\dot{m}} \quad (A34)$$

where $q_M := \frac{\dot{Q}_M}{\dot{m}}$.

Appendix A.3.1. Efficiencies of EM

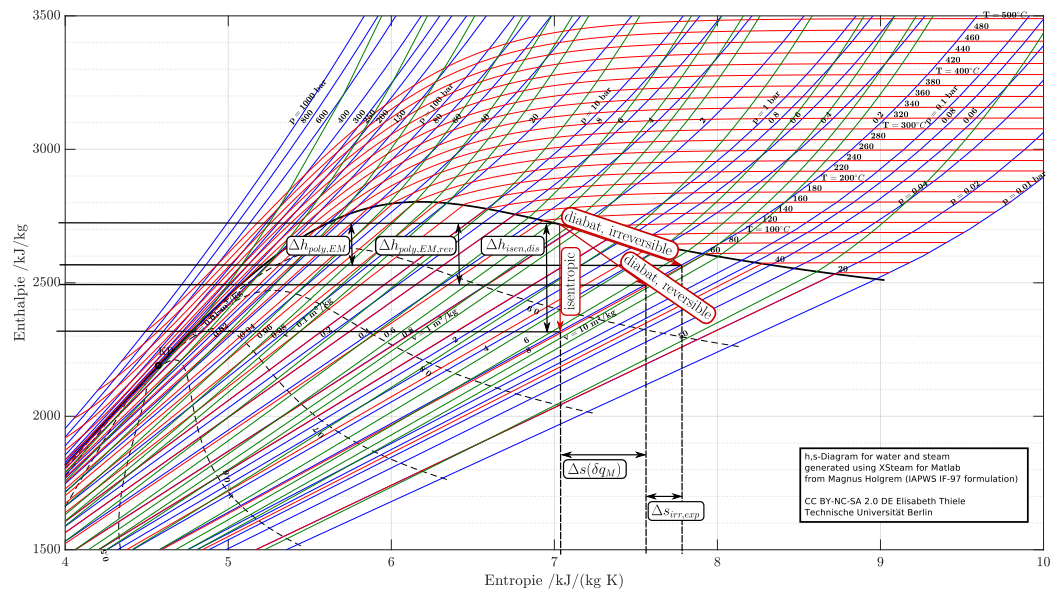


Figure A5. Illustration of enthalpy differences in the equations of expansion and compression device efficiencies, exemplified for the polytropic expansion.

$\eta_{i,EM/CM}$ is the inner efficiency of the expansion or compression machine and $\eta_{vol,EM/CM}$ is the volumetric efficiency, respectively, defined as the ratio of mass flow excluding the inner machine leakages to the mass flow including them (compare Figure A6):

$$\eta_{vol,EM} = \frac{\dot{m}}{\dot{m} + \dot{m}_{leak}} \quad (A35)$$

$$\eta_{vol,CM} = \frac{\dot{m} - \dot{m}_{leak}}{\dot{m}} \quad (A36)$$

The inner machine efficiency is defined as the ratio of real shaft work w^t to isentropic enthalpy difference along the machine Δh_{isen} . This equals to the product of the polytropic efficiency of expansion/compression $\eta_{poly,EM/CM}$ and the ratio of the isentropic to the polytropic ratio $\frac{v_{isen}}{v_{poly}}$:

$$\eta_{i,EM} = \frac{w_{dis}^t}{\Delta h_{isen,dis}} = \eta_{poly,EM} \cdot \frac{v_{isen,EM}}{v_{poly,EM}} \quad (A37)$$

$$\eta_{poly,EM} = \frac{w_{dis}^t}{\Delta h_{poly,EM,rev}} \quad (A38)$$

$$v_{isen,EM} = \frac{\Delta h_{poly,EM}}{\Delta h_{isen,dis}} \quad (A39)$$

$$v_{poly,EM} = \frac{\Delta h_{poly,EM}}{\Delta h_{poly,EM,rev}} \quad (A40)$$

$$\Delta h_{isen,dis} := h_{i,exp} - h(p_{exp,o}, s_{exp,i}) \quad (A41)$$

$$\Delta h_{poly,EM,rev} := h_{i,exp} - h(p_{exp,o}, s_{exp,i} + \frac{q_M}{\tilde{T}_{exp,i/o}}) \quad (A42)$$

$$\Delta h_{poly,EM} := h_{i,exp} - h_{o,exp} = w_{dis}^t - q_M \quad (A43)$$

Appendix A.3.2. Efficiencies of CM

Analogously, for compression:

$$\eta_{i,CM} = \frac{w_{ch}^t}{\Delta h_{isen,ch}} = \eta_{poly,CM} \cdot \frac{v_{isen,CM}}{v_{poly,CM}} \quad (A44)$$

$$\eta_{poly,CM} = \frac{\Delta h_{poly,CM,rev}}{w_{ch}^t} \quad (A45)$$

$$v_{isen,CM} = \frac{\Delta h_{isen,ch}}{\Delta h_{poly,CM}} \quad (A46)$$

$$v_{poly,CM} = \frac{\Delta h_{poly,CM,rev}}{\Delta h_{poly,CM}} \quad (A47)$$

$$\Delta h_{isen,ch} := h(p_{comp,o}, s_{comp,i}) - h_{comp,i} \quad (A48)$$

$$\Delta h_{poly,CM,rev} := h(p_{comp,o}, s_{comp,i} - \frac{q_M}{\tilde{T}_{comp,i/o}}) - h_{comp,i} \quad (A49)$$

$$\Delta h_{poly,CM} := h_{o,comp} - h_{i,comp} = w_{ch}^t - q_M \quad (A50)$$

where $\tilde{T}_{exp/comp,i/o}$ is the thermodynamic mean temperature of the heat transfer into the expansion machine/out of the compression machine. It should be noted that, defined in this way, the inner efficiencies $\eta_{i,EM/CM}$ are smaller than 1 for configurations A and B (adiabatic expansion/compression $q = 0 \rightarrow \Delta h_{poly,EM,rev} = \Delta h_{isen,dis} \rightarrow \frac{v_{isen,EM}}{v_{poly,EM}} = 1$) but eventually larger than 1 for configuration C (diabatic expansion and compression). The enthalpy differences are illustrated in Figure A5 for the polytropic expansion.

Appendix A.4. Heat-Transfer Circuit

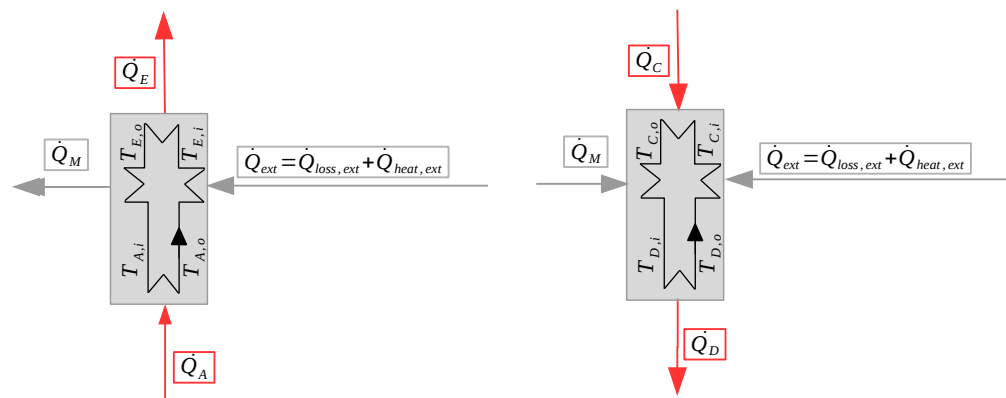


Figure A6. Energy balance of external heat-transfer circuit for discharging (left) and for charging (right).

The change in the internal energy of the heat-transfer circuit is neglected (small liquid volume). The external heat flows from and to the heat-transfer circuit are added up to $\dot{Q}_{ext}$, and the internal heat flow to the expander (heated expansion) or from the compressor (cooled compression) is named $\dot{Q}_M$.

Discharging

$$\dot{Q}_M + \dot{Q}_E = \dot{Q}_A + \dot{Q}_{ext} \quad (A51)$$

and:

$$\dot{Q}_{ext} = \dot{C}_{htf}(T_{E,i} - T_{A,o}), \quad (A52)$$

$$\dot{Q}_M = \dot{C}_{htf}(T_{E,o} - T_{A,i}), \quad (A53)$$

where $\dot{C}_{htf}$ is the heat capacity flow of the heat-transfer medium.

Charging

$$\dot{Q}_M + \dot{Q}_C = \dot{Q}_D + \dot{Q}_{ext} \quad (A54)$$

and:

$$\dot{Q}_{ext} = \dot{C}_{htf}(T_{C,i} - T_{D,o}), \quad (A55)$$

$$\dot{Q}_M = \dot{C}_{htf}(T_{D,i} - T_{C,o}). \quad (A56)$$

Appendix A.5. Combined Energy Balances—Absorber/Desorber and Expansion/Compression Machine

Discharging

The expanded vapor directly flows into the absorber, such that:

$$h_{Exp,o} = h_{A,i}.$$

Combining Equations (A33) and (A27), we find:

$$\begin{aligned} \dot{Q}_A = & \dot{m}(h_{Exp,i} - h_E(T_E) + l(x, T_A) - c_{pE}\Delta T_{dis} - w^t) \\ & - C_A(x) \frac{dT_A}{dt} + \dot{Q}_M - \dot{Q}_{loss,A} - \dot{Q}_{loss,EM} \end{aligned} \quad (A57)$$

The vapor from the evaporator directly enters the expansion machine, such that:

$$h_{Exp,i} = h_{E,o}(T_E, \chi).$$

Equation (A57) can be written as follows:

$$\begin{aligned} \dot{Q}_A = & -P^t + \dot{m} \cdot (\chi \Delta h^{lv} + l_A(x, T_A) - c_{pE}\Delta T_{dis}) \\ & - C_A(x) \frac{dT_A}{dt} + \dot{Q}_M - \dot{Q}_{loss,A} - \dot{Q}_{loss,EM} \end{aligned} \quad (A58)$$

Charging

The desorbed vapor directly flows into the compression device, such that:

$$h_{D,o} = h_{compr,i}.$$

Combining Equations (A34) and (A28), we find:

$$\begin{aligned} \dot{Q}_D = & \dot{m}(h_{compr,o} - h_C(T_C) + l(x, T_D) + c_{pC}\Delta T_{ch} - w^t) \\ & + C_D(x) \frac{dT_D}{dt} + \dot{Q}_M + \dot{Q}_{loss,CM} + \dot{Q}_{loss,D} \end{aligned} \quad (A59)$$

The compressed vapor enters the condenser directly:

$$h_{comp,o} = h_{C,i}.$$

With Equation (A8), Equation (A59) can be written as follows:

$$\begin{aligned} \dot{Q}_D = -P^t + \dot{m} \left(\Delta h^{lv} + \frac{w_{rev,comp}^t \cdot v_{isen,CM}}{\eta_{th,ch}} + l_A(x, T_D) + (c_{p,C} - c_{p,C}^{\prime\prime}) \Delta T_{ch} \right) \\ + C_D(x) \frac{dT_D}{dt} + \dot{Q}_M + \dot{Q}_{loss,CM} + \dot{Q}_{loss,D} \end{aligned} \quad (A60)$$

Appendix B. Deduction of the Guiding Differential Equations

Appendix B.1. Case (A)

In the case of a directly coupled system, we find:

$$\dot{Q}_A = \dot{Q}_E = \dot{Q}_{dis} \quad (A61)$$

$$\dot{Q}_D = \dot{Q}_C = \dot{Q}_{ch} \quad (A62)$$

Using the heat-transfer characteristic of the system:

$$\dot{Q}_{dis} = k \cdot A \cdot \Delta T_{dis} \quad (A63)$$

$$\dot{Q}_{ch} = k \cdot A \cdot \Delta T_{ch} \quad (A64)$$

We find, for the A/D balances (Equations (A58) and (A60) under neglect of EM/CM heat losses):

$$\frac{dT_A}{dt} = -\frac{k \cdot A}{C_A(x)} \Delta T_{dis} + \frac{\chi \Delta h^{lv}(T_E) + l_A(x, T_A) - c_{p,E} \Delta T_{dis}}{C_A(x)} \dot{m} - \frac{P_{dis}^t}{C_A(x)} - \frac{\dot{Q}_{loss,A}}{C_A(x)} \quad (A65)$$

$$\frac{dT_D}{dt} = \frac{k \cdot A}{C_D(x)} \Delta T_{ch} - \frac{\Delta h^{lv}(T_C) + l_A(x, T_D) + \frac{w_{rev,comp}^t \cdot v_{isen,CM}}{\eta_{th,ch}} + \Delta c_{p,C}^{lv} \cdot \Delta T_{ch}}{C_D(x)} \dot{m} \quad (A66)$$

$$+ \frac{P_{ch}^t}{C_D(x)} - \frac{\dot{Q}_{loss,D}}{C_D(x)} \quad (A67)$$

where $\Delta c_{p,C}^{lv} := c_{p,C} - c_{p,C}^{\prime\prime}$.

From the E/C balances (Equations (A7) and (A11)):

$$\frac{dT_E}{dt} = \frac{k \cdot A}{C_E(x)} \Delta T_{dis} - \frac{\chi \Delta h^{lv}(T_E)}{C_E(x)} \dot{m} - \frac{\dot{Q}_{loss,E}}{C_E(x)} \quad (A68)$$

$$\frac{dT_C}{dt} = -\frac{k \cdot A}{C_C(x)} \Delta T_{ch} + \frac{\Delta h^{lv}(T_C) + \frac{w_{rev,comp}^t \cdot v_{isen,CM}}{\eta_{th,ch}}}{C_C(x)} \dot{m} - \frac{\dot{Q}_{loss,C}}{C_C(x)} \quad (A69)$$

The guiding differential equation for $\Delta T_{dis/ch}$ can be found by subtracting Equation (A68) from (A65) for discharging and Equations (A67) and (A69) for charging and replacing the power output/input:

$$\text{for discharging: } P^t = \dot{m} \cdot \eta_{vol} \cdot w_{rev}^t(x(t), T_A) \cdot \eta_{i,EM} \cdot \eta_{th} \quad (A70)$$

$$\text{for charging: } P^t = \dot{m} \cdot \frac{1}{\eta_{vol}} \cdot w_{rev}^t(x(t), T_D) \cdot \frac{1}{\eta_{i,EM}} \cdot \frac{1}{\eta_{th}} \quad (A71)$$

Appendix B.2. Cases (B) and (C)

In case of an external heat-transfer circuit with (case C) and without (case B) the expansion/compression device connected, the heat flows at A/E and D/C are not equal anymore. The thermodynamic mean temperatures in the heat-transfer circuit $T_{A,ext}/T_{D,ext}$

and $T_{E,ext}/T_{C,ext}$ are approximated by the arithmetic mean values of the in- and outlets of the heat exchangers:

$$T_{A/D,ext} \approx \frac{1}{2}(T_{A/D,i} + T_{A/D,o}) \quad (A72)$$

$$T_{E/C,ext} \approx \frac{1}{2}(T_{E/C,i} + T_{E/C,o}) \quad (A73)$$

Discharging

For discharging, the heat flows are calculated as:

$$\dot{Q}_A = k_A A_A (T_A - T_{A,ext}) \quad (A74)$$

$$\dot{Q}_E = k_E A_E (T_{E,ext} - T_E) \quad (A75)$$

Rearranging Equations (A52) and (A53) after $T_{E,i}$ and $T_{E,o}$, respectively, and inserting them into Equation (A73), we find:

$$T_{E,ext} = \frac{1}{2} \left(\frac{\dot{Q}_{ext}}{\dot{C}_{htf}} + T_{A,o} + \frac{\dot{Q}_M}{\dot{C}_{htf}} + T_{A,i} \right), \quad (A76)$$

and with Equations (A72) and (A74):

$$T_{E,ext} = \frac{1}{2} \left(\frac{\dot{Q}_{ext}}{\dot{C}_{htf}} + \frac{\dot{Q}_M}{\dot{C}_{htf}} \right) + T_A - \frac{\dot{Q}_A}{k_A \cdot A_A}. \quad (A77)$$

Finally, inserting into Equation (A75), the relation of evaporator and absorber heat flow can be found:

$$\dot{Q}_E = k_E \cdot A_E \left[(T_A - T_E) + \frac{1}{2} \frac{\dot{Q}_{ext} + \dot{Q}_M}{\dot{C}_{htf}} - \frac{\dot{Q}_A}{k_A \cdot A_A} \right]. \quad (A78)$$

Now, to obtain the temperature change in the evaporator, the absorber heat flow is replaced by the energy balance of the heat-transfer circuit, Equations (A51) and (A78) is rearranged after the evaporator heat flow. Then, the evaporator heat flow is replaced by the energy balance around the evaporator, Equation (A7), and we find:

$$\begin{aligned} \frac{dT_E}{dt} = & \frac{\frac{k_E \cdot A_E \cdot k_A \cdot A_A}{k_E \cdot A_E + k_A \cdot A_A}}{C_E(x)} \left[\Delta T_{dis} + \left(\frac{1}{2\dot{C}_{htf}} + \frac{1}{k_A \cdot A_A} \right) \dot{Q}_{ext} + \left(\frac{1}{2\dot{C}_{htf}} - \frac{1}{k_A \cdot A_A} \right) \dot{Q}_M \right] \\ & - \frac{\chi \Delta h^{lv}}{C_E(x)} \dot{m} - \frac{\dot{Q}_{loss,E}}{C_E(x)} \end{aligned} \quad (A79)$$

For the temperature change in the absorber, analogously, the evaporator heat flow is replaced by the energy balance of the heat-transfer circuit, Equation (A51), and Equation (A78) is rearranged after the absorber heat flow. Then, the absorber heat flow is replaced by the energy balance around the absorber, Equation (A58):

$$\begin{aligned} \frac{dT_A}{dt} = & - \frac{\frac{k_E \cdot A_E \cdot k_A \cdot A_A}{k_E \cdot A_E + k_A \cdot A_A}}{C_A(x)} \left[\Delta T_{dis} + \left(\frac{1}{2\dot{C}_{htf}} - \frac{1}{k_E \cdot A_E} \right) \dot{Q}_{ext} + \left(\frac{1}{2\dot{C}_{htf}} + \frac{1}{k_E \cdot A_E} \right) \dot{Q}_M \right] \\ & + \frac{\chi \Delta h^{lv} + l_A(x) - c_{p,E} \Delta T_{dis}}{C_A(x)} \dot{m} - \frac{P^t}{C_A(x)} - \frac{\dot{Q}_{loss,A}}{C_A(x)} \end{aligned} \quad (A80)$$

Charging

For charging, the heat flows are calculated as:

$$\dot{Q}_D = k_D A_D (T_{D,ext} - T_D) \quad (A81)$$

$$\dot{Q}_C = k_C A_C (T_C - T_{C,ext}) \quad (A82)$$

We proceed analogously to the discharging phase by rearranging Equations (A55) and (A56) after $T_{C,o}$ and $T_{C,i}$ and inserting them into Equation (A73):

$$T_{C,ext} = \frac{1}{2} \left(\frac{\dot{Q}_{ext}}{\dot{C}_{htf}} + T_{D,o} + T_{D,i} - \frac{\dot{Q}_M}{\dot{C}_{htf}} \right) \quad (A83)$$

and with Equations (A72) and (A81), we find:

$$T_{C,ext} = \frac{1}{2} \left(\frac{\dot{Q}_{ext}}{\dot{C}_{htf}} - \frac{\dot{Q}_M}{\dot{C}_{htf}} \right) + T_D + \frac{\dot{Q}_D}{k_D \cdot A_D} \quad (A84)$$

Inserting this into Equation (A82) gives:

$$\dot{Q}_C = k_C \cdot A_C \left[(T_C - T_D) - \frac{1}{2} \frac{\dot{Q}_{ext} - \dot{Q}_M}{\dot{C}_{htf}} - \frac{\dot{Q}_D}{k_D \cdot A_D} \right] \quad (A85)$$

For the temperature change in the condenser, the desorber heat flow is replaced by the energy balance around the external heat-transfer circuit, Equation (A54), and rearranged for the condenser heat flow. Then, the condenser heat flow is replaced by the energy balance around the condenser, Equation (A11):

$$\begin{aligned} \frac{dT_C}{dt} = & -\frac{\frac{k_C \cdot A_C \cdot k_D \cdot A_D}{k_D \cdot A_D + k_C \cdot A_C}}{C_C(x)} \left[\Delta T_{ch} - \left(\frac{1}{2\dot{C}_{htf}} + \frac{1}{k_D \cdot A_D} \right) \dot{Q}_{ext} + \left(\frac{1}{2\dot{C}_{htf}} - \frac{1}{k_D \cdot A_D} \right) \dot{Q}_M \right] \\ & + \frac{\Delta h^{lv} + \Delta h_{sh}}{C_C(x)} \dot{m} - \frac{\dot{Q}_{loss,C}}{C_C(x)} \end{aligned} \quad (A86)$$

For the temperature change in the desorber, the condenser heat flow is replaced by the energy balance around the external heat-transfer circuit, Equation (A54), and the desorber heat flow by the energy balance around the desorber, Equation (A60):

$$\begin{aligned} \frac{dT_D}{dt} = & \frac{\frac{k_C \cdot A_C \cdot k_D \cdot A_D}{k_D \cdot A_D + k_C \cdot A_C}}{C_D(x)} \left[\Delta T_{ch} - \left(\frac{1}{2\dot{C}_{htf}} - \frac{1}{k_C \cdot A_C} \right) \dot{Q}_{ext} + \left(\frac{1}{2\dot{C}_{htf}} + \frac{1}{k_C \cdot A_C} \right) \dot{Q}_M \right] \\ & - \frac{\Delta h^{lv} + \Delta h_{sh} + l_A(x) + c_{p,C} \Delta T_{ch}}{C_D(x)} \dot{m} + \frac{P^t}{C_D(x)} - \frac{\dot{Q}_{loss,D}}{C_D(x)} \end{aligned} \quad (A87)$$

Appendix C. Normalization of Thermal Masses with Salt Mass

$$\frac{C_{A/D}(x)}{m_{salt}} = \frac{C_{A/D,P}}{m_{salt}} + c_{p,A} \frac{1}{x} \quad (A88)$$

$$\frac{C_{E/C}(x)}{m_{salt}} = \frac{C_{E/C,P}}{m_{salt}} + c_{p,E/C} \left(\frac{1}{\underbrace{x_{discharged}}_{\frac{m_{A/D,discharged}}{m_{salt}}}} - \underbrace{\frac{1}{x}}_{\frac{m_{A/D}(x)}{m_{salt}}} + \frac{1}{\underbrace{x_{charged}}_{\frac{m_{A/D,charged}}{m_{salt}}}} - \frac{1}{\underbrace{x_{charged} + \delta x_{buffer,EC}}_{\frac{m_{A/D,charged} - m_{buffer,EC}}{m_{salt}}}} \right) \quad (A89)$$

A buffer term is introduced to avoid the complete dry-out of the evaporator at the end of discharging. Therefore, instead of an empty evaporator, there is a certain rest mass of

water $m_{buffer,EC}$. In order to stay in the nomenclature of salt mass fraction, it is introduced in the above equation with $\delta x_{buffer,EC}$. If $m_{buffer,EC} = 0$, we obtain the simpler and more obvious expression:

$$\frac{C_{E/C}(x)}{m_{salt}} = \frac{C_{E/C,P}}{m_{salt}} + c_{p,E/C} \left(\frac{1}{x_{discharged}} - \frac{1}{x} \right) \quad (A90)$$

The ratio of thermal masses of the periphery to the entire salt mass $\frac{C_{A/E,P}}{m_{salt}}$ should get smaller the larger the storage is. However, it is neglected here; therefore, we assume a rather large system with a small surface-to-volume ratio. For small plants, this should not be neglected.

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