Thermodynamic analysis of chemical heat pumps

Jonas Obermeier [a, b], Karsten Müller [a, b, *], Wolfgang Arlt [a, b]

[a] Institute of Separation Science & Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany
[b] Energie Campus Nürnberg, Fürther Str. 250, 90429 Nürnberg, Germany

ARTICLE INFO

ABSTRACT

Thermal energy storages and heat pump units represent an important part of high efficient renewable energy systems. By using thermally driven, reversible chemical reactions a combination of thermal energy storage and heat pump can be realized. The influences of thermophysical properties of the involved components on the efficiency of a heat pump cycle is analysed and the relevance of the thermodynamic driving force is worked out. In general, the behaviour of energetic and exergetic efficiency is contrary. In a real cycle, higher enthalpies of reaction decrease the energetic efficiency but increase the exergetic efficiency. Higher enthalpies of reaction allow for lower offsets from equilibrium state for a default thermodynamic driving force of the reaction.

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1. Introduction

One of the main challenges in the establishment of renewable energy systems is to overcome the decoupled energy supply and demand. In case of heat utilization, efficient heat storage units and heat transformation systems must be developed. A highly efficient storage system is characterized by low energy losses, high energy densities and a small difference between loading and unloading temperatures. In case of heat transformation units, efficiency depends on feasible temperature rise and corresponding necessary energy input.

Thermally driven, reversible chemical reactions can combine the principles of a storage and transformation system in a single unit. In this kind of thermochemical storage system, the enthalpy of reaction $\Delta^R h$ is stored as chemical energy in the products of the reaction [1] and determines the order of magnitude of storage density. Based on thermodynamic considerations, the temperature of chemical equilibrium, often called turning temperature T^*, and enthalpy of reaction $\Delta^R h$ are linked by changes in entropy $\Delta^R s$ between reactants and products [2]. The turning temperature T^* indicates the temperature level of chemical equilibrium.

$$T^* = \frac{\Delta^R h}{\Delta^R s} \qquad (1)$$

The aim of high storage densities at moderate temperatures can thus be realized by high reaction entropies. This thermophysical requirement is fulfilled by most endothermic decomposition reactions of solids: A reactant $AB_{(s)}$ decomposes into a solid $A_{(s)}$ and a vapor phase $B_{(g)}$ through the supply of external energy Q.

$$\nu_{AB} \cdot AB_{(s)} + Q \rightleftharpoons \nu_A \cdot A_{(s)} + \nu_B \cdot B_{(g)} \qquad (2)$$
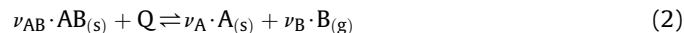
After separation of products, the solid $A_{(s)}$ can be stored under ambient conditions and enables long-term, low loss heat storage. The variety of different reaction types like dehydration of salt hydrates, dehydrogenation of metal hydrides, dehydration of metal hydroxides or decarboxylation of metal carbonates [1] enables a wide range of temperatures and applications.

The reaction equilibrium determines the operation range of a gas-solid thermochemical storage system. In equilibrium state, the change of Gibbs free energy Δg is zero. Under the assumptions of immiscibility of solid compounds and an ideal gas behavior of compound B the Gibbs free energy Δg is equal to Gibbs free energy of reaction $\Delta^R g$. Neglecting molar volumes of the solids, the pressure-temperature relation of the reaction equilibrium for the decomposition reaction (equation (2)) can be described by equation (3). The term P/P^+ defines the ratio of system pressure P to

reference pressure P^+ of thermophysical data, R is the universal gas constant and ν_B the stoichiometric coefficient of component $B_{(g)}$.

$$\ln\left(\frac{P}{P^+}\right) = -\frac{\Delta^R h(T, P^+)}{\nu_B R} \cdot \frac{1}{T^*} + \frac{\Delta^R s(T, P^+)}{\nu_B R} \quad (3)$$

The temperature-dependency of enthalpy and entropy of reaction must be regarded to achieve an accurate prediction of reaction equilibrium. In contrast to equation (3), in the literature the reaction enthalpy and entropy are often regarded as temperature-independent parameters (e.g. C_1, C_2). The validity range of the resulting equation (4) should be verified for each reaction system individually.

$$\ln(P) = C_1 \cdot \frac{1}{T^*} + C_2 \quad (4)$$

The possibility to influence the reaction temperature by changing the reaction pressure enables the usage of gas-solid reactions in a thermodynamic cycle. In such a chemical heat pump, forward and reverse reactions are forced to occur at different temperature levels in order to transform the temperature of a thermal energy source. Those systems consist of four units which are working at three different temperature levels. An evaporator at low temperatures (T_L), a condenser and a synthesis reactor at middle temperatures (T_M) and an endothermic decomposition reactor (formation of $A_{(s)}$ and $B_{(g)}$) at a high temperature level (T_H). For a heat pump system of type I [3] there are two different operation modes: heating (heat pump = HP) and cooling (refrigerator = R). In both cases a high temperature heat source is needed as an energy input. A HP provides heat at medium temperature and R supplies cold at a low temperature level. In this study all considerations are focused on HP operation mode.

Fig. 1 illustrates the basic operation of a gas-solid chemical heat pump system of type I. The curve labelled with L/V corresponds to the vapor-pressure of component B which is determined by Clausius–Clapeyron equation. The S/SV curve is the reaction equilibrium of decomposition reaction described by equation (3). The cycle starts at point 1 with low pressure (P_L) and low temperature (T_L) level. In this first step, the liquid phase evaporates and the component $B_{(g)}$ is available for the solid $A_{(s)}$ (at T_M and P_L) for the

exothermic composition reaction (point 3). The product $AB_{(s)}$ must be heated up to T_H and the pressure must be increased to P_H ($3 \rightarrow 4$). At this point 4, the endothermic decomposition reaction is initiated by a high temperature heat source. The released component $B_{(g)}$ is isobarically cooled down and condensates at T_M in point 2. In the last step, the liquid is cooled down and the pressure is decreased to P_L. At the same time the temperature of solid $A_{(s)}$ is reduced to T_M in order to be available for the next cycle.

As already mentioned, this gas-solid equilibrium is monovariant with the result that by fixing one temperature or pressure value, all operation points of the cycle are fixed. For example, presetting the evaporator temperature T_L, the evaporator pressure P_L is directly determined for a specific reaction system. Because of the isobaric heating of the vapor ($1 \rightarrow 3$) and the monovariant equilibrium of the gas-solid reaction, the temperature T_M can be iteratively calculated using equation (3). The temperatures of the composition reaction and condensation are equal and thus, the high pressure level P_H is determined by the vapor-pressure curve. Based on the pressure level P_H the temperature required for decomposition T_H can be calculated with the monovariant gas-solid equilibrium [4].

For the assessment of different reaction systems, energetic and exergetic efficiency analyses of the heat pump systems are necessary. The energetic efficiency is called coefficient of performance (COP). A short-cut method for the determination of the COP is described by equation (5). For this consideration just the enthalpy of reaction $\Delta^R h$ and enthalpy changes during the vapor-liquid phase change Δh^{LV} are taken into account [3]. For a proper heat and mass balance the stoichiometric coefficient of component B must be part of the COP calculation and is regarded in equation (5) as a factor in the enthalpy change Δh^{LV}. The reference states of the compounds are chosen referring to the defined phases in equation (2) and thus, the enthalpy of sublimation is part of the enthalpy of reaction $\Delta^R h$ and is not separately listed in the following equations.

$$COP_{HP} \approx \frac{\left|\Delta h^{LV}(T_M) + \Delta^R h(T_M)\right|}{\Delta^R h(T_H)} \quad (5)$$

For a more accurate investigation it is necessary to consider the preheating and cooling steps between the reaction and phase change which can be calculated with the specific heat capacities $c_{p,i}$.
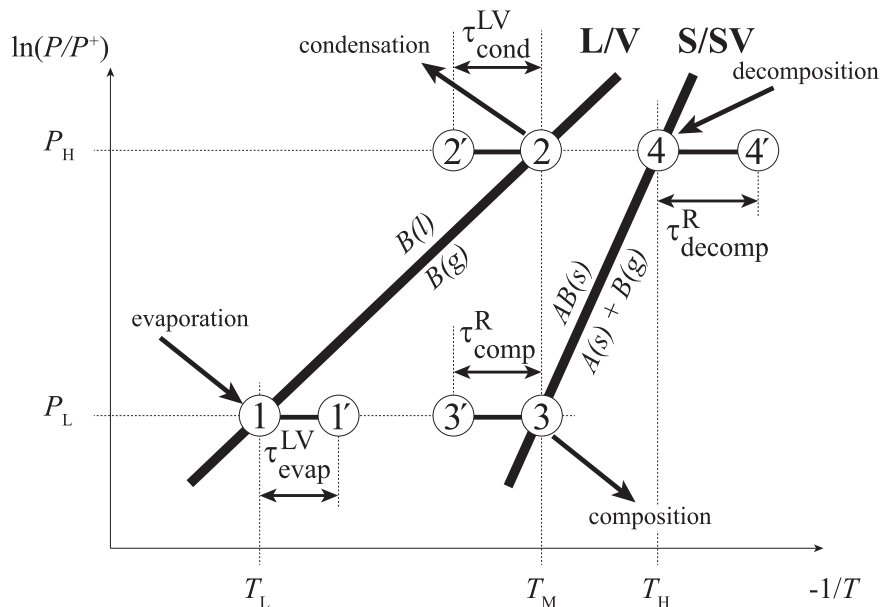

Fig. 1. Basic operation of a gas-solid chemical heat pump system of type I.