BOND ENERGY

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Contents

Summary

The forming or loosing of chemical bounds takes place with simultaneous heat release or heat consumption. We call this bond energy. By opening the bond this energy is "stored" in the "potential bond", i.e. the reactants, and, consequently, can be released again by closing the bond. Thus it can be used for technical heat storage if the reaction is not too irreversible.

We will discuss the different processes and materials which can be utilized first from a fundamental point of view. We will then see that not only storage of heat is possible but also transformation of the temperature of this stored heat, heat pumping, cold production, and even storing of work. Finally, some practical examples and an outlook for applictions will be given.

1. Basic Considerations and Definitions

1.1.   Definition of Bond Energy Storage

We define "bond energy" in the scope of heat storage systems as a latent thermal energy which is set free in processes which are based on chemical reactions or the like. These processes comprise:

- simple reversible chemical reactions of gases
- chemical reactions of gases which are reversed using several steps
- solid-gas chemical reactions like calcination
- forming of complex compounds like ammoniates
- forming of metal hydrides
- other kinds of heterogeneous evaporation
- adsorption of a gas into a solid
- absorption of a gas into a liquid
- forming of gas hydrates (clathrates)

It is seen immediately, that in all cases more than one species is involved in the storage process. This feature makes the storage of bond energy unique with respect to all other forms of heat storage, as, e.g., latent heat storage of phase change materials.

Still, the case of storage of latent heat of phase change is very similar to the storage of bond energy. There are two equations to describe the effect in the case of latent heat storage, which are:

A (1st phase) $\leftarrow$ A (2nd phase) $+$ ΔH (heat consumed due to melting or evaporation)
A (1st phase) $\rightarrow$ A (2nd phase) $+$ ΔH (heat released due to solidification or condensation)

In the case of bond energy we can formulate for the two different species A and B (see Figure 1):

$A + B$ $\leftarrow$ $A\,B$ $+$ ΔH (heat consumed, decomposition)
$A + B$ $\rightarrow$ $A\,B$ $+$ ΔH (heat released, synthesis)

The reaction may or may not feature an additional phase change. Due to the fact that at least two different species have to be involved, there arises the possibility to separate the two partners after the storing (heat consuming) reaction.

Thus the release of heat which would be caused by the reversion of the reaction (synthesis) is made impossible, which is an important distinction from all other forms of energy storage. The heat release can be controlled totally arbitrarily.

The only problem is that the separation has to be accomplished in a technically feasible way, or that the reverse reaction is kinetically blocked and can be controlled via catalysis. Both ways are being considered.
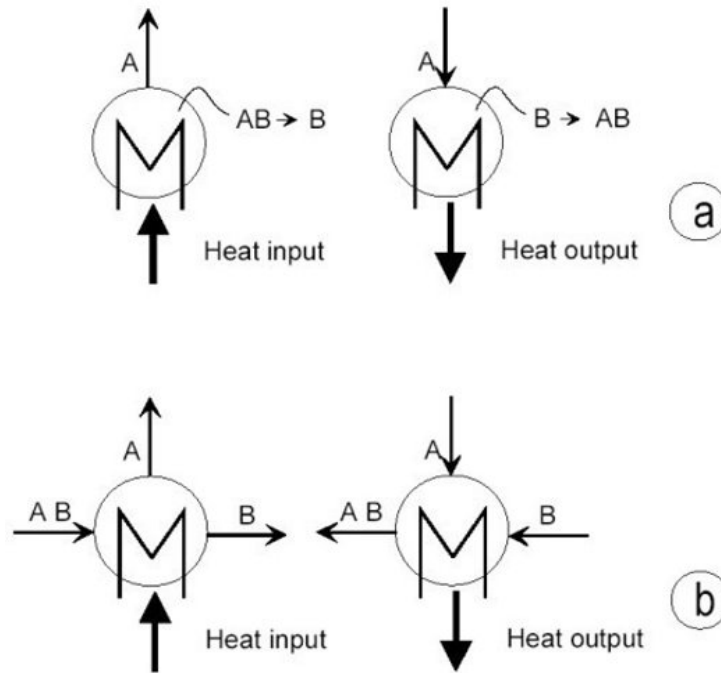
Figure 1: Principle of heat storage (a: one partner B localized, b: all partners flowing)

Proceeding further on the path we laid out above, we discuss under the term of bond energy all heat storage systems which involve two or more separate working media in such a way that these working media are being combined in order to release heat and are separated by consuming heat, thus bringing forth the storing effect.

The two reactions are not governed by external parameters like the temperature alone but are controlled by the user. Two cases are shown in Figure 1: In the first case (a) the reacting partner B is localized and the other reacting partner A is extracted from the reactor when loading the store and brought into the reactor when the stored heat is released. This is a typical arrangement for partner B being a solid. In the second case (b) the reactor is a kind of heat exchanger which is passed continuously by the reactants when in operation. In the loading phase the combined partners flow into the system but they leave the reactor separated or are being separated afterwards.

In the heat release phase both partners enter the reactor and leave it combined. Case b will be typical for fluid media. Of course, the separation is more easily accomplished if the state of partners A and B is different, e.g., A being a gas and B being a liquid or solid.

1.2. Scale of the Energetic Effect

In Table 1 the order of magnitude of the energy which is related to different effects which may be used for heat storage is compared and tabulated in rising order (ref. Alefeld, 1975a).

The different kinds of bond energy as classified here, beginning with heterogeneous evaporation, range in the order of phase change energy and above.

Physical effect	Related energy	Remark
Sensible Heat	3 R ΔT	ΔT: temperature swing between max. loading temp. and min. unloading temp.
Melting	$1.1 R T_m$ to $4.5 R T_m$	T_m: melting temperature
Vaporizing	$9 R T_v$ to $13 R T_v$	T_v: boiling temperature at 1 bar
Heterogenous evaporation	$15 R T_v$ to $18 R T_v$	T_v: boiling temperature at 1 bar
Simple chemical bond	50 R T to 220 R T	T: room temperature
Double bond	70 R T to 290 R T	T: room temperature
Triple bond	370 R T to 430 R T	T: room temperature

Table 1: Energetic comparison of different physical effects (R is the gas constant)

Medium	Volume related energy density [kJ/ltr]	Remark
Rock	50	Sensible heat, 20K
Water	84	Sensible heat, 20K
Ice	330	Latent heat
Zeolite + steam	500	Sorption*
Ammonia vapor	806	Latent heat
CaO + steam	900	Reaction*
CaO + CO_2	2000	Reaction*
Steam	2165	Latent heat

*: Weight and volume of only the solid partner is being considered. Only the heat effect of the reaction and not that of the condensation of the produced vapor (see Fig. 6) is taken into account.

Table 2: Comparison of energy density of different storage media

One of the most important parameters for heat storage systems is the volumetric or gravimetric energy density, i.e. the amount of heat which can be stored in a given volume or at a given weight, respectively. In Table 2, typical storage densities are compared for practical systems. Numbers are given for the storage materials solely, because the densities of the systems depend on the design to a large extent. Only condensed matter is being considered.

From the table it can be concluded that in technical terms of energy density storing of bond energy is similar to storing latent heat of evaporation. However, the given numbers are theoretical limits for the energy density only; one of the most important challenges is to design a system in such a way that in addition to the energy density the power density is large also.

In this respect, great care has to be given to the heat conductivity of the materials and the heat transfer coefficients in the total system. The theoretical preference to storing bond energy in many cases is overcompensated by technical problems. It has to be recalled that a high power density can always be achieved when large temperature gradients are being applied. Consequently, this aspect is much more dependent on the system design than on

the storage materials which are being used.

2. Heat Storage and Heat Transformation

One of the most interesting features of heat storage using bond energy as compared to other physical effects is the inherent possibility for heat transformation. Heat transformation means shifting a given amount of heat from one temperature to another.

A heat exchanger does this in an irreversible way, from high temperature to low. A heat pump lifts heat from low temperature to high temperature and, in the limiting case, may perform a reversible heat transformation.

This is not totally different from the case of phase change energy, because the respective two reactions do not have to take place at the same temperature. Nevertheless, with two temperature levels alone no reversible transformation is possible without additional work input.

However, in the case of using bond energy four different temperature levels can be involved as will be explained later. With these four temperature levels, a lot of different possibilities for reversible heat transformation exist.

Of course, it is important that the temperature can be influenced easily for the purpose of heat transformation. In the case of vaporizing the variation of the phase change temperature is very easy to accomplish by changing the vapor pressure. The same holds for most of the reactions used for storing bond energy. Examples will be shown below.

In Figure 2 the basic difference between reversible heat storage (a → b) and reversible heat transformation (a → c or a → d) is depicted. In order to store heat in a reversible way the two reactions, decomposition and synthesis, take place under the same constraints (e.g., the pressure).

 Just one parameter has to be changed slightly such that the equilibrium is on one or the other side of the reaction. Then the heat will be consumed or set free at the same temperature, except for small deviations to drive the reaction. In the fully reversible case, these deviations tend to zero. This is shown in Figure 2a (loading) and Figure 2b (unloading).

If the heat is to be transformed to another temperature, we have to change one of the possible constraints. In many cases this will be the pressure because the equilibrium temperature is dependent on the pressure as indicated in the figure by the equilibrium line.

Then, the unloading may be performed at a higher temperature (Figure 2c) or a lower temperature (Figure 2d). Of course, additional energy flows are required both in order to accomplish the pressure change and in order to close the entropy balance. In the examples, we will see real cases of such kind of heat transformers.
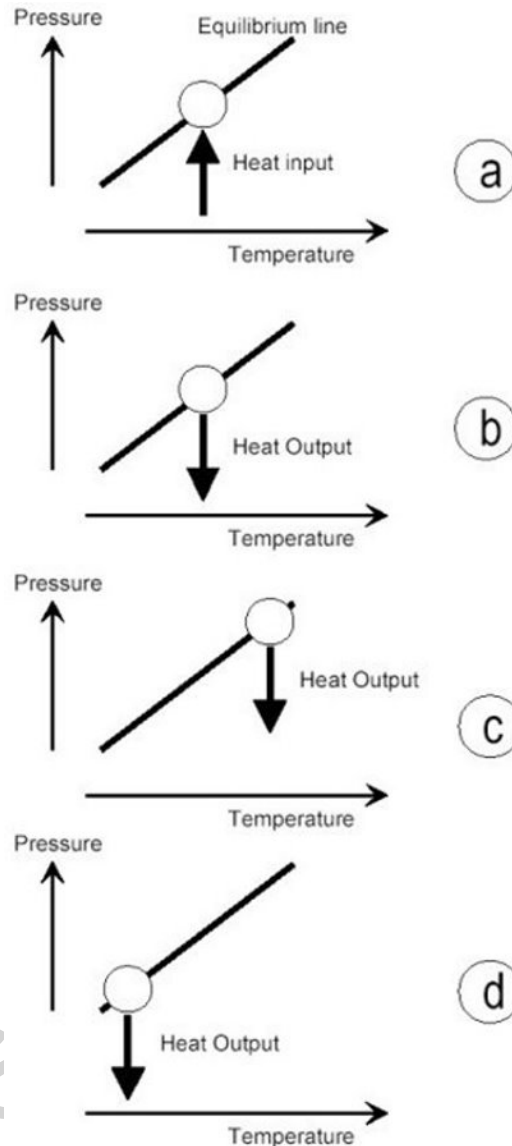
Figure 2: Principle of heat storage (a: loading, b: unloading) and heat transformation (a: loading, c unloading at higher temperature, d: unloading at lower temperature.

Due to the fact that with the storage of bond energy heat transformation becomes possible, we can also envisage the storage of work by bond energy: we can load the store with heat but unload it by extracting work in addition or vice versa (see Figure 8). This feature is not discussed frequently; a practical example is reported in the chapter about absorption systems.

3. Examples of Storage Systems and Applications

There are many rationales to choose a reacting pair for heat storage: temperature and pressure range, thermodynamic efficiency (storage efficiency), experience, complexity in handling, safety, environmental concerns, and, above all, cost. Very similar considerations hold for heat transformation devices. Consequently, at this point the discussion of working pairs which are currently applied or under close consideration for

heat transformation may be useful, because some systems for heat transformation are state of the art whereas the storage of bond energy is not.

Albeit the large number of possibilities, in the heat transformation applications only liquid sorption systems and only two working pairs can be considered to be mature state of the art: $H_2O/LiBr$ for water chillers and NH_3/H_2O for refrigeration (Ziegler, 1999). In the discussion on new pairs, we can distinguish two lines of research: one tries to change the characteristics of those well-known pairs. The other line tries to come up with new working pairs.

Within the second line, there are two possibilities: first, organic pairs often have been proposed. This interest prevails, although on a low level. But it seems to be quite sure that organics are a good choice if for any reason the classical pairs do not work in a specific application. Today they still do not play a significant part.

A more radical solution is the switch to solid sorbents. Zeolite continuously attracts a lot of attention, but Silica-Gel chillers are commercially available. Moreover, the basic research seems to be more active in the field of Silica-gel, as well as in the field of ammonia salts. All these solid sorption systems may well be applied to storage, because they feature an inherent storage capability due to the batch type of process (see below).

In this chapter some of the few examples of pilot applications as well as laboratory experiments for storage will be reported on. There will be systems with mere heat storage features, systems which feature heat transformation, and systems which incorporate the transformation to work also. It has to be repeated, that up to now no storage system is commercially available to a significant extent.

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Biographical Sketch

Felix Ziegler studied Mechanical Engineering at Technische Universität München, Germany. After having received his Diploma he moved to the faculty of physics where he continued his studies under the auspices of the late Prof. Georg Alefeld. There, in 1991, he got his Doctor's degree for a dissertation about the combination of compression and absorption cooling processes.

Felix Ziegler stayed at the Technische Universität München as senior researcher and lecturer. In 1995 he moved to the Bavarian Center for Applied Energy Research (ZAE Bayern). He was head of the division for „Energy conversion and storage" for six years. In 2001 Felix Ziegler was appointed full professor at the Institute for Energy Engineering of Technische Universität Berlin.

The main research interest of Felix Ziegler is sorption cooling and heat transformation devices, energy storage, heat and mass transfer, and energy systems engineering.

Felix Ziegler was born in 1955 in Hamburg, Germany. Today he lives in Glienicke, north of Berlin, together with his wife and son.