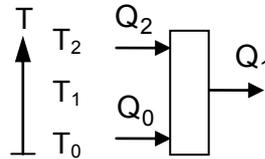


## CYCLE BASICS OF THERMALLY DRIVEN HEAT PUMPS

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### 1 FUNDAMENTALS

Thermally driven heat pumps (TDHP) work at three temperature levels. Driving heat  $Q_2$  is supplied at a high temperature level. Useful cold (cooling operation) or low temperature heat (heating operation)  $Q_0$  is supplied at a low temperature level. The sum of the heat supplied is released at a medium temperature level.  $Q_1$  is the useful heat in heating operation. In cooling operation, it is usually released to the environment. However, medium and low temperature heat can also be used simultaneously for heating and cooling purposes.



**Figure 1: Temperature levels of thermally driven heat pumps for heating and cooling**

In principle, all closed cycle TDHP types can be operated in heating and cooling mode. However, when we talk about thermally driven heat pumps, we usually refer to absorption or adsorption heat pumps. Having the highest process efficiencies (coefficient of performance, COP) they are far more widespread than TDHP processes like steam jet, double organic Rankine (ORC), thermoacoustic, thermoelectric, Stirling, Vuilleumier, Pulse tube, or Gifford-McMahon processes. These cycles are mainly discussed for applications with additional specific requirements such as, for example, very low useful temperatures. There are also combined (compression-sorption hybrid cycles, see Ziegler 1991) or successive heat and mechanically driven processes like Rankine and vapor compression.

The efficiency of TDHPs is defined by

$$\text{COP}_c = \frac{\dot{Q}_0}{\dot{Q}_2} \text{ for cooling operation,} \quad (1)$$

$$\text{COP}_h = \frac{\dot{Q}_1}{\dot{Q}_2} = 1 + \text{COP}_c \text{ for heating operation and} \quad (2)$$

$$\text{COP}_{h+c} = \frac{\dot{Q}_1 + \dot{Q}_0}{\dot{Q}_2} = 1 + 2 \cdot \text{COP}_c \text{ for combined heating and cooling operation.} \quad (3)$$

However, it is better to use  $\text{COP}_c$  or  $\text{COP}_h$  only, even for the combined operation, in order not to confuse the thermodynamic meaning.

The electrical energy input of TDHPs often is negligibly small. Otherwise, a second number, the electrical COP ( $\text{COP}_{el}$ ), can be used in order to distinguish it from the thermal COP ( $\text{COP}_{th}$ ).

## 2 ABSORPTION HEAT PUMPS

Just as in the conventional compression heat pump process, in the absorption heat pump process useful heat is produced by condensation of a refrigerant. Prior to that, in the evaporator (E) the refrigerant is evaporated at a lower pressure using a low temperature heat source (see Figure 2). However, in the absorption heat pump process the refrigerant vapor is not compressed by a mechanically driven compressor to overcome the pressure difference but is instead pumped in a liquid state. The electrical energy input required is very small due to the considerably lower specific volume of liquid compared to vapor refrigerant.

For suction of the vapor refrigerant of the evaporator a suitable liquid, the absorbent, is used. During the absorption process in the absorber (A) heat is generated and has to be released. It is used for heating purposes as the condensation heat. Therefore, the ratio of useful heat  $Q_1$  to the heat from the low temperature heat source  $Q_0$  is larger than in compression heat pumps. To liquefy the refrigerant at the evaporation pressure, but at a higher temperature, the effect of boiling point elevation due to the addition of a second liquid to the refrigerant is used.

During the absorption process, the absorbent is diluted and, therefore, has to be regenerated to maintain its absorption capability. To this end, the diluted solution is pumped to the higher pressure level into the desorber (D) where heat is supplied to boil off the refrigerant. The vapor refrigerant is condensed in the condenser (C) and throttled to the evaporator pressure, and the refrigerant cycle can start again. The concentrated solution is also throttled and flows back to the absorber where it can absorb the vapor refrigerant anew. Another heat exchanger, the so-called solution heat exchanger (SHX), is added into the solution circuit to increase the efficiency of the process by means of internal heat exchange.

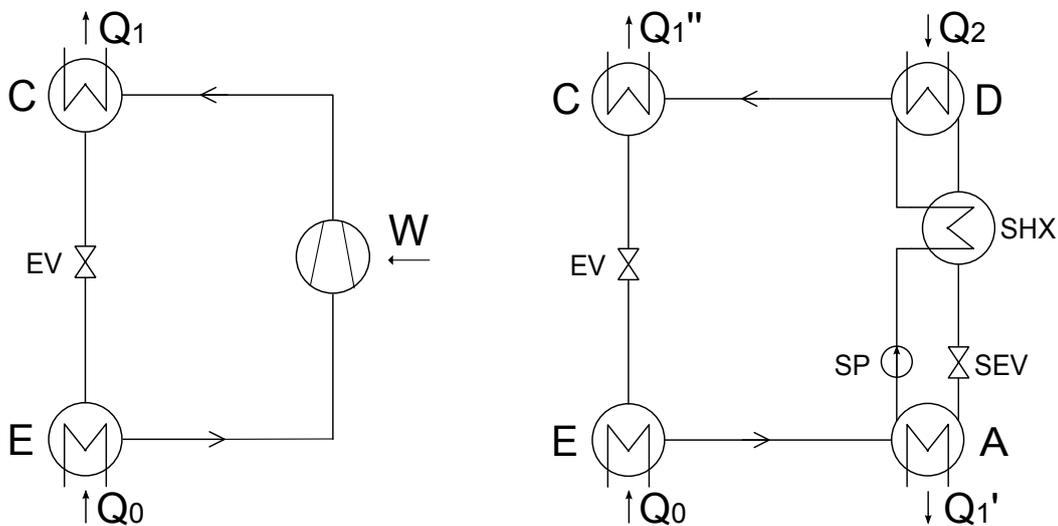
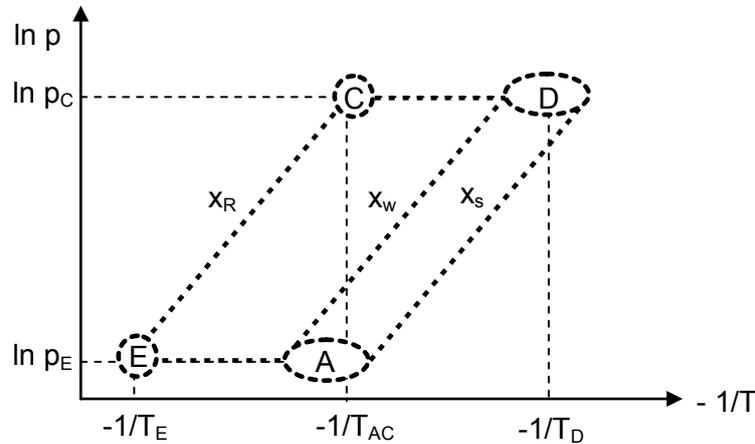


Figure 2: Compression (left) and absorption (right) heat pump cycle

The absorption heat pump cycle is usually displayed in a vapor pressure diagram (Figure 3) where due to the  $\ln p/-1/T$  scaling the boiling curves are almost straight lines. In this diagram, the two pressure and the three temperature levels can be recognized easily.  $x_w$  and  $x_s$  are the absorbent mass fractions of the weak (diluted) and the strong (concentrated) solution. Their difference is called concentration difference  $\Delta x$ . The absorbent mass fraction is defined as the ratio of absorbent mass to the total mass of solution. Ideally, the volatility of the absorbent is small as compared to that of the refrigerant. In this case, the absorbent mass fraction of the refrigerant  $x_R$  is 0, i.e. there is no absorbent in the refrigerant cycle between

condenser and evaporator. Otherwise, a rectification is needed. Another characteristic number is the solution circulation ratio (pump rate)  $f$  defined as

$$f = \frac{\dot{m}_w}{\dot{m}_R} = \frac{x_s}{\Delta x} \quad (4)$$



**Figure 3: Absorption heat pump cycle in the  $\ln p/-1/T$  diagram**

The basic cycle described so far is the single effect cycle. The reversible COP,

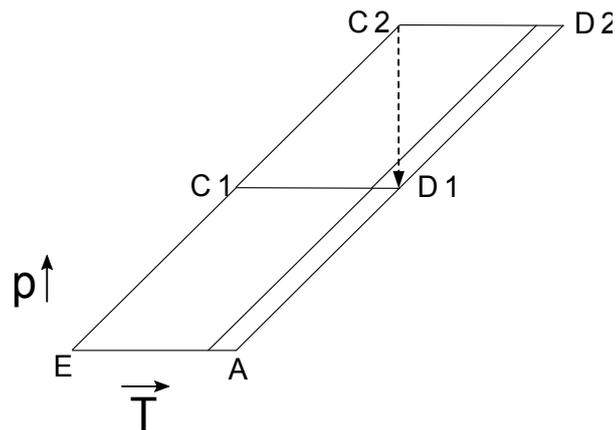
$$\text{COP}_{\text{rev,c}} = \frac{r}{r+1} \quad (5)$$

$$\text{COP}_{\text{rev,h}} = 1 + \frac{r}{r+1} \quad (6)$$

of a single effect cooling cycle is always below 1 and that of a single effect heat pump cycle always below 2 as long as the specific heat of solution  $l$  is in the order of 10% of the heat of evaporation  $r$ . This is the case for all working pairs known to date.

To achieve higher cycle efficiencies, to decrease the required driving temperature level, or to achieve high temperature glides of the driving heat medium, several modifications of this cycle have been developed, namely multi effect or multi lift cycles (e.g. Ziegler et al. 1993). The term "effect" is used especially for cooling applications to describe how often the heating unit supplied is used to achieve a regeneration effect and thus a useful cooling effect. The term "lift" is used to describe the multiple by which the temperature lift between the heat sink and the heat source is higher than the temperature thrust between the driving heat and the heat sink. This is equivalent to the number of heating units supplied per useful cooling unit. Multi effect cycles are used to increase the efficiency (coefficient of performance, COP). Multi lift cycles make it possible to drive the process at low temperatures (e.g. low temperature waste heat). In this case, a reduction of the COP is accepted.

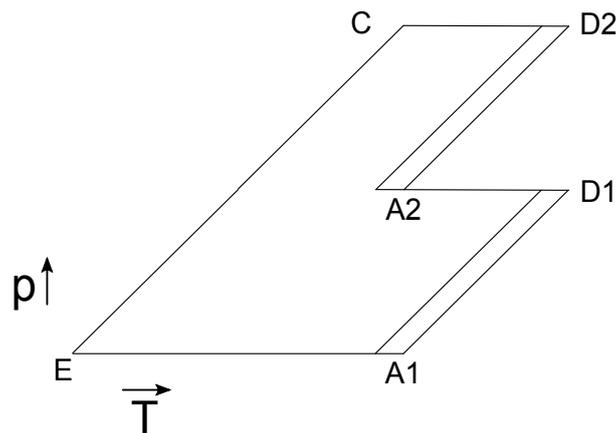
Figure 4 presents a schematic of a double effect absorption cycle in the vapor pressure diagram. A  $\text{COP}_c$  of 1.0 to 1.3 can be achieved due to an internal heat exchange. Triple or quadruple effect cycles are also possible if high temperature driving heat is available and limiting factors like corrosion problems can be solved.



**Figure 4: Double effect absorption heat pump cycle in the  $\ln p/-1/T$  diagram**

The double effect principle is also possible with an internal heat transfer when the temperature glide in the absorber and desorber overlaps (high concentration difference between strong and weak solution). In this case, the heat of absorption is used to partly regenerate the solution in the desorber (generator). This principle is called generator-absorber heat exchange (GAX) (Altenkirch 1913/1914, Scharfe et al. 1986).

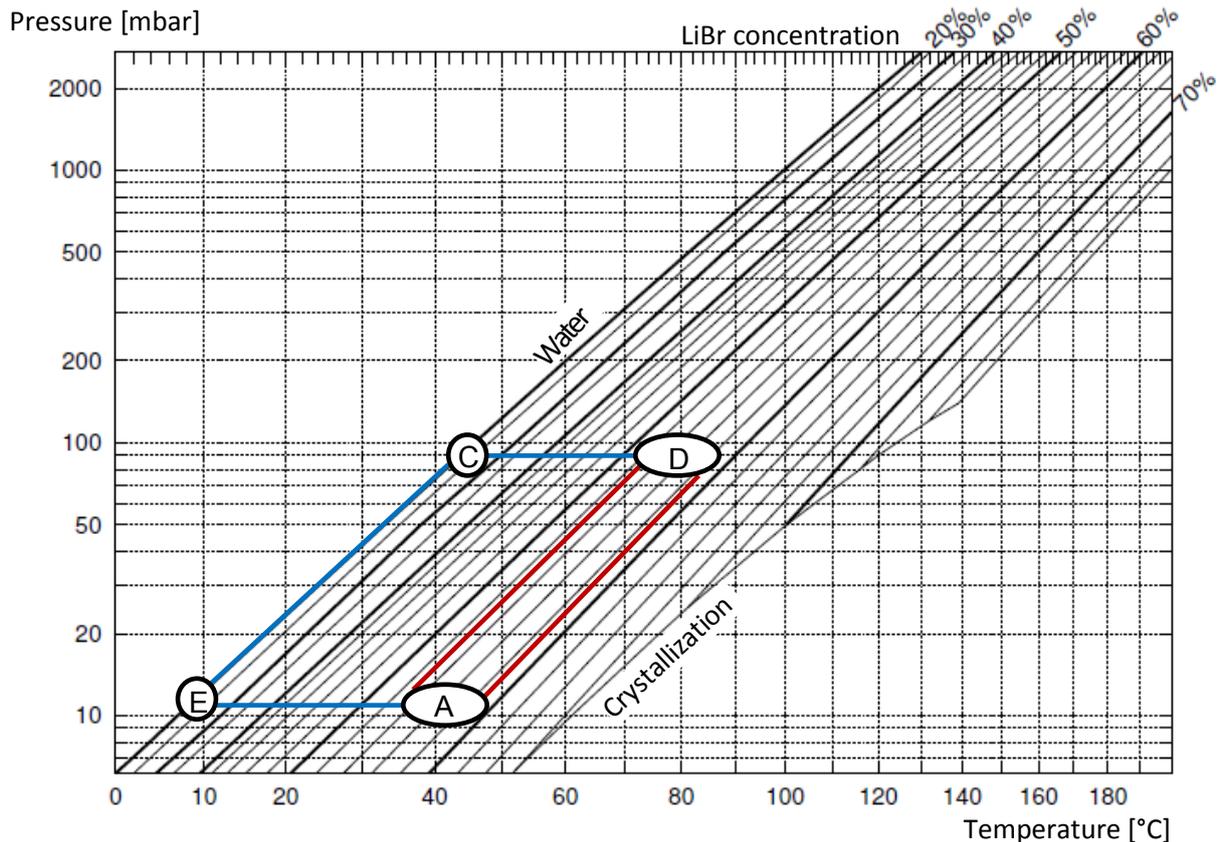
In Figure 5, a typical double lift cycle is represented. Cooling COPs of up to 0.4 are achieved.



**Figure 5: Double lift absorption heat pump cycle in the  $\ln p/-1/T$  diagram**

Although many working pairs for absorption heat pumps and cooling machines have been suggested over the last half century, only two prevail: water/LiBr and ammonia/water.

Water has a high latent heat, is chemically stable, non-toxic, environmentally-neutral, and economical. A drawback, however, is the low vapor pressure which requires a vacuum-tight construction of the vessels. The application is limited by the freezing temperature of  $0^{\circ}\text{C}$ . However, a depression of the freezing point is possible by adding substances like salts (Kojima 2003, Richter 2007, Kühn 2008). Aqueous LiBr solution has a negligible vapor pressure, a low viscosity and is non-toxic. The formation of crystals at high absorbent concentration is unfavorable (see crystallization line in Figure 6) and limits the possible temperature lift, i.e. the difference between low and medium temperature level. Nevertheless, the working pair water/LiBr permits the highest energetic and economic efficiency using simple, well-engineered, and relatively compact systems.



**Figure 6: Absorption heat pump cycle plotted over the vapor pressure lines of water/LiBr (Feuerecker 1994)**

Ammonia, in contrast, is toxic, and is flammable and explosive in air for some concentrations. Depending on the charge, special safety precautions are necessary. The vapor pressure is high (see Figure 7). Therefore, pressure vessels are needed, and the solution pump requires more energy. Water has a significant vapor pressure as compared to ammonia and, consequently, for high temperature lift a rectification or a liquid bleed is required which reduces the process efficiency. One advantage of ammonia/water is that the solution does not crystallize. Ammonia/water permits the generation of very low refrigeration temperatures down to  $-40^{\circ}\text{C}$  and the use of high heating supply (heat pump mode) or cooling water temperatures (cooling mode) if the driving temperature is high enough. Ammonia/water systems are slightly more complex, not as efficient as water/LiBr systems and need more auxiliary power. However, as opposed to water/LiBr heat pumps, it is possible to use compact and cost efficient plate heat exchangers instead of tube bundles.

In recent years, new working pairs based on ionic liquids as absorbents have been investigated (Radspieler and Schweigler 2011, Schneider et al. 2011). Ionic liquids are considered to have a high potential to overcome the weaknesses of the prevalent pairs.

A modification of the absorption heat pump process described so far is the diffusion absorption heat pump process developed by the Swedes Platen and Munters as early as 1922. The idea is to introduce an auxiliary inert gas (e.g. helium) which is able to compensate the refrigerant partial pressure difference between condenser and evaporator and desorber and absorber, respectively. The result is a unique total pressure in the whole machine. In Figure 8, the third cycle, the thermosyphon driven auxiliary gas circulation, can be seen. The big advantage of this technology is that a simple bubble pump with no moving parts is able to circulate the  $\text{NH}_3/\text{water}$  solution. This principle has been used a millionfold for absorber refrigerators in the hotel or camping business.

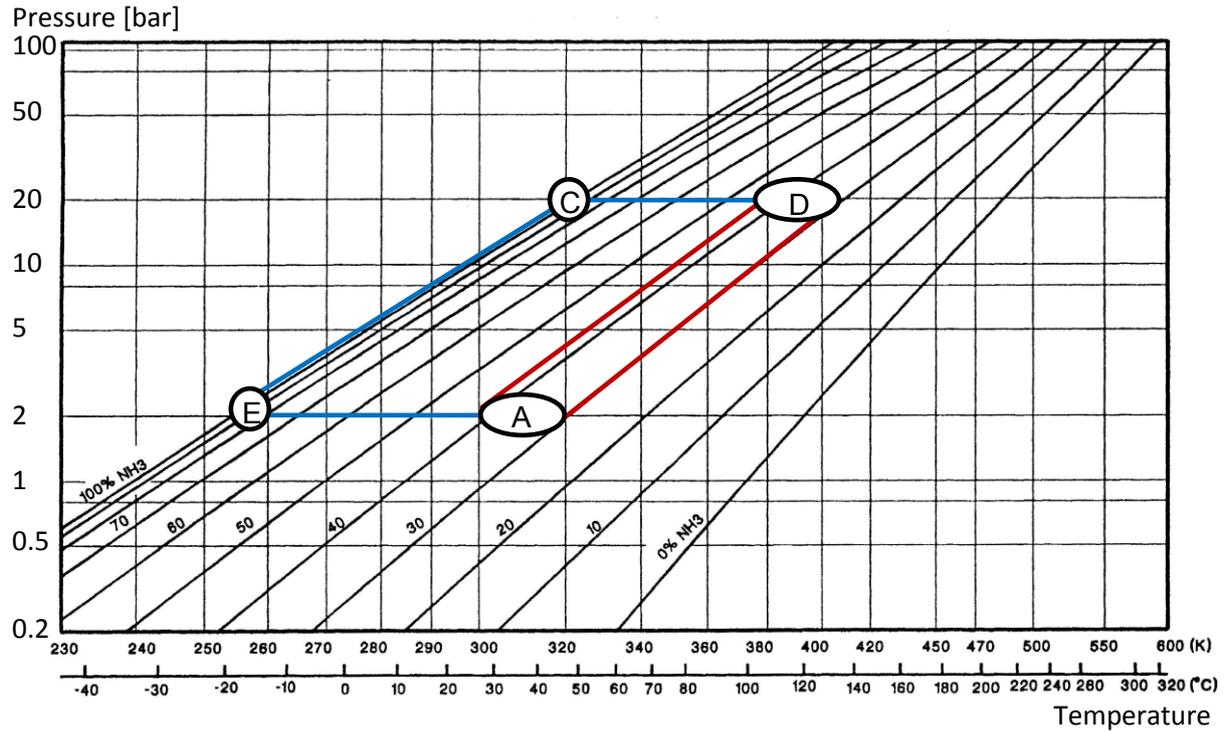


Figure 7: Absorption heat pump cycle plotted over the vapor pressure lines of  $\text{NH}_3/\text{water}$  (Ziegler and Trepp 1984)

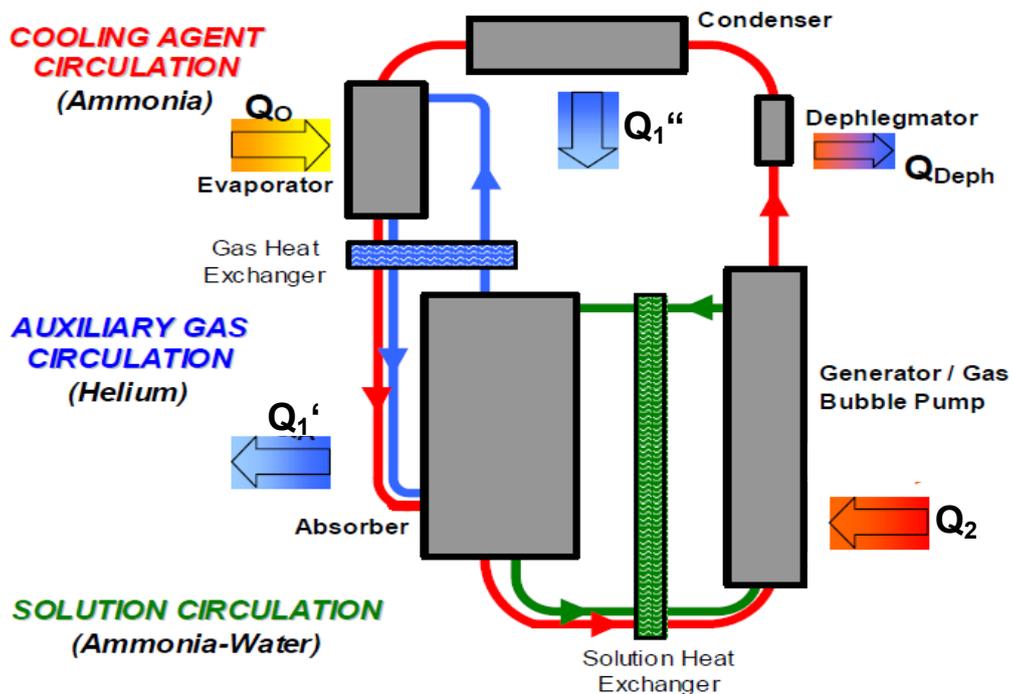
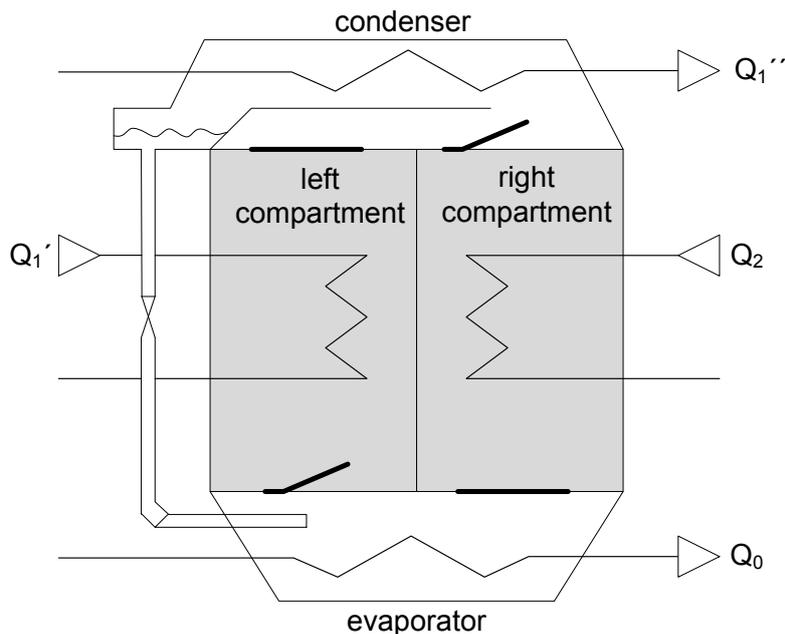


Figure 8: Functional principle of a diffusion absorption heat pump (Jakob and Eicker 2002)

### 3 ADSORPTION HEAT PUMPS

Unlike absorption where the refrigerant is absorbed in a liquid sorbent, in the case of adsorption the refrigerant is adsorbed in the pores of a solid sorbent. The adsorption heat pumping cycle is thermodynamically similar to the absorption cycle. It consists of the same main heat exchangers: evaporator, condenser, and a heat exchanger for adsorption and desorption. Unlike the absorption process where the liquid absorbent is pumped between absorber and desorber, adsorption is a discontinuously working process as the solid adsorbent cannot easily be moved from one vessel to the other. Adsorption and desorption can occur successively in the same vessel. However, to ensure a reasonably continuous useful heating or cooling effect, two so-called reactors are usually used and operated in counter-phase. Figure 9 shows a typical construction of an adsorption heat pump.



**Figure 9: Typical adsorption heat pump design (on the basis of Henning 2004a)**

In Figure 10, a typical adsorption process is explained. In phase 1, the refrigerant evaporates and is taken up by the adsorbent in the right compartment. The adsorption heat has to be removed by an external heat carrier and is used for heating purposes (heat pump mode) or rejected to the environment (cooling mode). Simultaneously, in the left compartment the adsorbent regeneration takes place. Heat is supplied to desorb the refrigerant. The refrigerant vapor flows to the condenser where it is condensed, and then throttled and returned to the evaporator like in the conventional compression or absorption process. Usually, flaps ensure an autonomous connection or disconnection of adsorber/desorber and evaporator/condenser. In phase 3, the same processes occur with the difference that adsorption takes place in the left and desorption in the right compartment.

When changing the phases there is a short period without cold/heat production followed by a peak in the heat/cold production. Over time, adsorption capability decreases. Cycling time is therefore a more important control parameter compared to the pump rate in absorption heat pumps. While short cycles tend to provide higher useful heating or cooling power density, process efficiency is mostly higher with longer cycle times. It is possible to have either fixed or variable cycle times, depending on a defined minimum useful heat or cold delivered.

In order to reduce the decrease in efficiency due to the lack of a solution heat exchanger, there are several concepts for heat recovery of adsorbent, heat exchanger, and vessels

when shifting the phase. In commercial applications, both compartments are usually connected thermally (heat recovery) or directly (mass recovery) during the switching phases 2 and 4. Nevertheless, internal heat recovery is not as effective as it is for absorption heat pumps, resulting in lower process efficiencies.

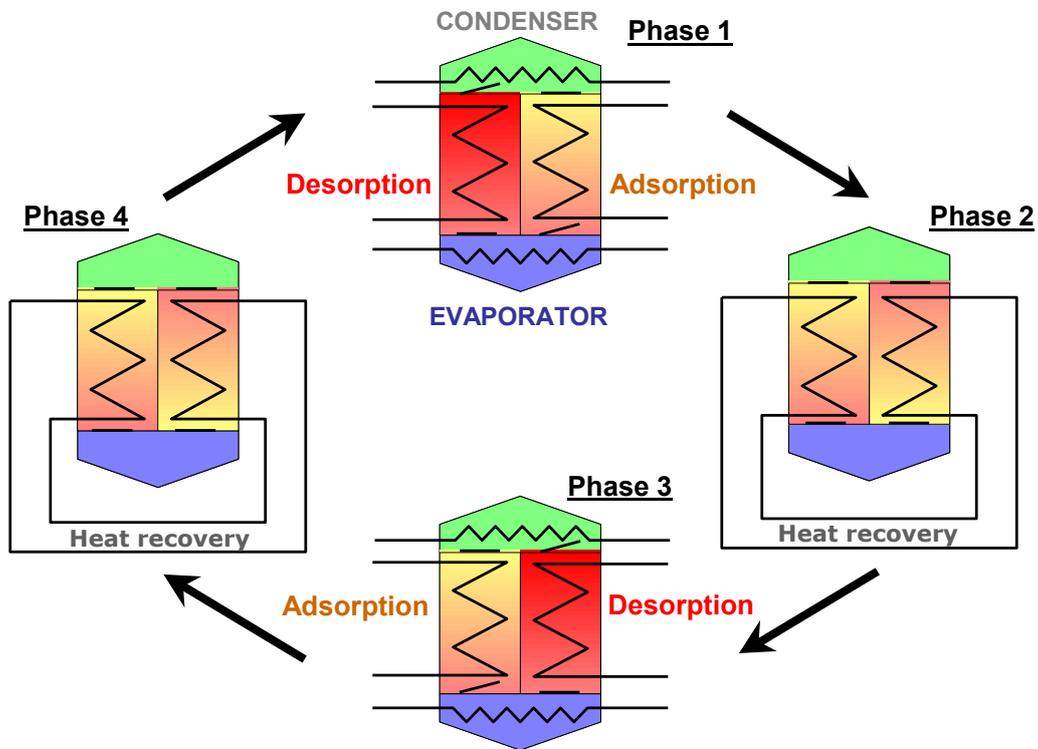


Figure 10: Adsorption cycle with heat recovery (on the basis of Henning 2004b)

In order to increase the performance of the machines, some more sophisticated configurations have been developed, such as thermal wave (Shelton et al. 1989, see Figure 11) or multi-bed (e.g. Saha et al. 2003). As for absorption heat pumps, cycles have been adapted for lower driving temperatures (e.g. Saha et al. 2003).

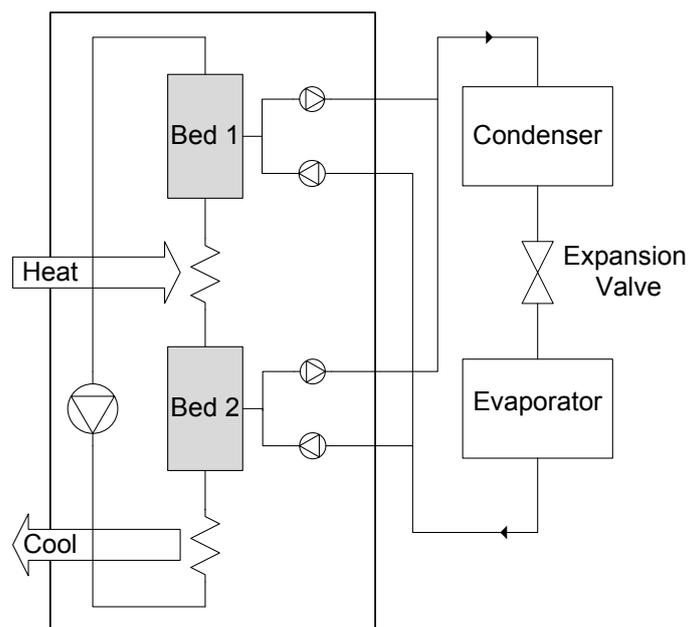


Figure 11: Thermal wave adsorption heat pump (Critoph 1999)

A suitable adsorbent is a porous, solid material with a high internal surface. The most common adsorption heat pump working pairs are water/silica gel, water/zeolite, ammonia/activated carbon and methanol/activated carbon.

It is standard, like for the absorption heat pump process, to represent the adsorption process in a  $\ln p-1/T$  diagram. Figures 12 and 13 show the diagrams of water/silica gel Grace 125 and water/zeolite Z13X, two typical examples.

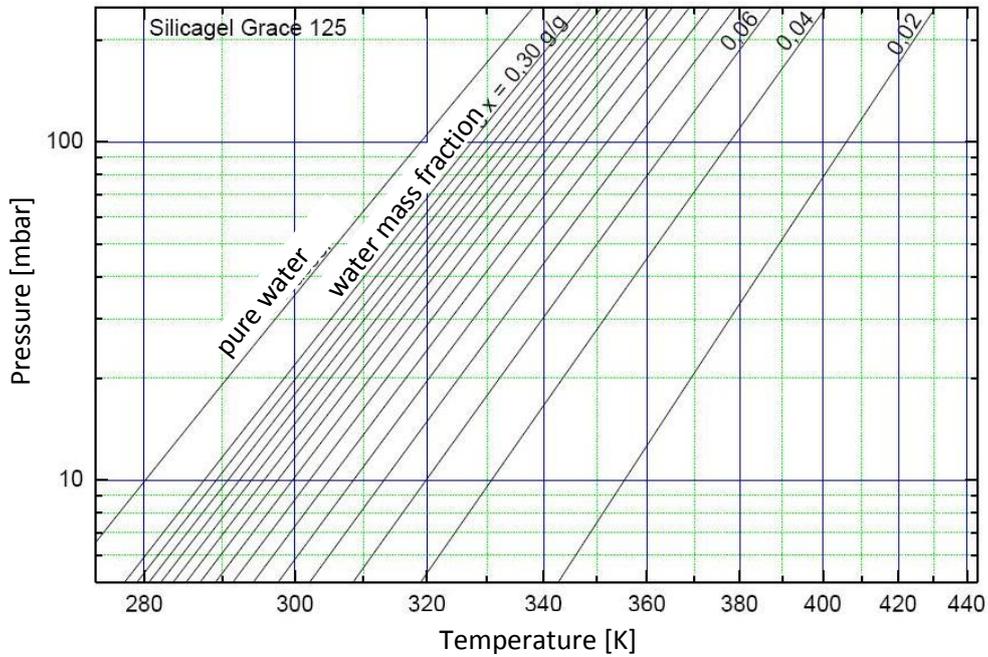


Figure 12:  $\ln p-1/T$  diagram of silica gel Grace 125 (Jahnke 2008 on the basis of Nuñez 2001)

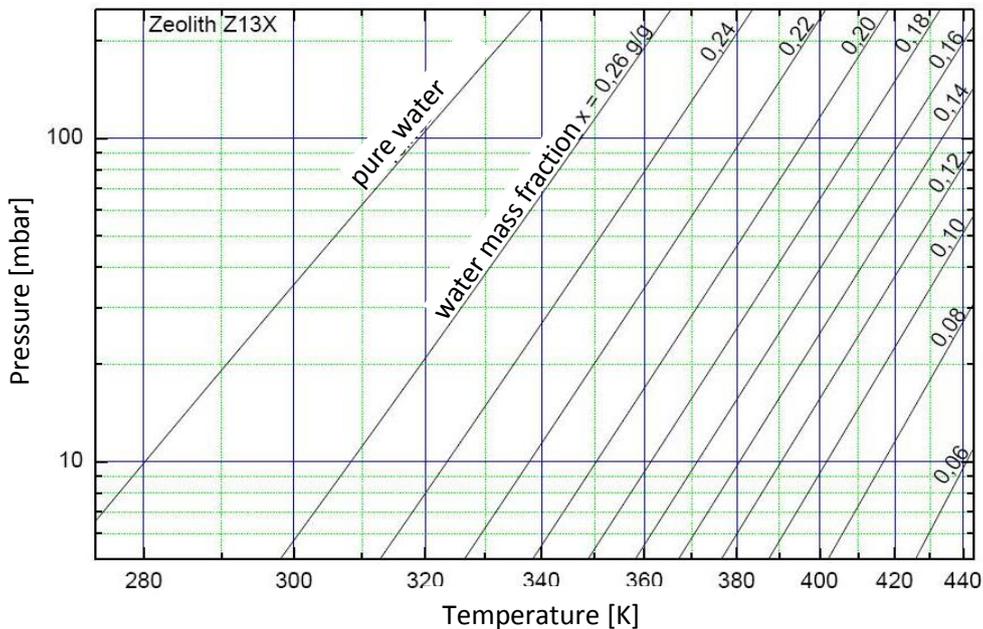


Figure 13:  $\ln p-1/T$  diagram of zeolite Z13X (Jahnke 2008 on the basis of Nuñez 2001)

Isosteres describe all boiling states with the same mass fraction  $x$  (vapor pressure/boiling curves). High refrigerant uptake in certain temperature ranges can be realized where isosteres are narrow. From a comparison of Figures 12 and 13, it can be concluded that

silica gel Grace 125 is more suitable for low temperature lifts and low driving temperatures while zeolite Z13X fits for higher temperature lifts and higher driving temperatures. Today, like in the case of ionic liquids for absorption heat pumps, adsorbents are expected to be tailor-made by the manufacturers in accordance to the user requirements (e.g. suitable for low driving temperatures or suitable for high temperature lifts).

#### **4 COMPARISON**

Water/LiBr absorption heat pumps offer the highest thermal efficiencies. Water/LiBr chillers have been produced and operated in large numbers and a wide power range for many decades. Nevertheless, the temperature lift is limited by the potential crystallization of the sorbent. Ammonia/water absorption heat pumps can be operated with environmental heat sources below zero degrees (e.g. air or ground collectors) or employed for refrigeration. Market available ammonia/water heat pumps supply domestic hot water up to 70°C. The drawback is the high upper pressure level and the high energy consumption of the circulation pump that requires special design. Adsorption heat pumps are not limited in the temperature lift by these constraints. However, their efficiency is generally lower. The discontinuously working process involves fluctuating outlet temperatures of the hydraulic circuits.

It is very often said that adsorption chillers need lower driving temperatures than absorption chillers. Ziegler and Lamp derived as early as 1996 by physical means that for identical boundary conditions and vanishing concentration difference between strong and weak solution or loaded and unloaded adsorbent the theoretical minimum driving temperature is almost the same for absorption and adsorption systems which were used frequently at that time. For real but fixed pump rates absorption heat pumps require even lower driving temperatures than adsorption heat pumps. Kühn et al. (2005) presented a small scale water/LiBr absorption chiller with 55°C minimum driving hot water temperature (50% part load) with nearly no efficiency drop compared to the design point.

Adsorption heat pumps operate without moving components like pumps. The opening and closing of the flaps is self-regulating or controlled by valves. In terms of power density, no clear statement for the preference of absorption or adsorption can be given yet. It seems today that adsorption units of around 10 kW can be very compact, but for higher capacity, absorption systems are supposed to be more compact and more efficient.

Adsorption machines are less affected by motion, but absorption heat pumps can also be applied successfully in the automotive or shipping sector as reported by Safarik et al. (2011). Motion can even be used to increase the heat and mass transfer (e.g. Gilchrist 2002).

Academic research activities, today, focus more on adsorption heat pumps as there is still potential of process optimization in order to increase the performance. Absorption cooling machines are technically mature, although the use as a heat pump could certainly be intensified. One major next step for both absorption and adsorption heat pumps is the increase of power density and reduction of manufacturing costs. In future, moreover, it could be crucial whether the tailor-making of adsorbents or adsorbents leads to better results.

#### **5 SYSTEMS**

To be operated, the sorption heat pump has to be connected to a high temperature heat source, a low temperature heat source, and a medium temperature heat sink. Possible system configurations are presented in Figures 14 (heat pump mode) and 15 (cooling mode).

The reject heat in heat pump operation is used to provide room heating or domestic warm water with a temperature level of typically 20 to 70°C. As for compression heat pumps the low temperature heat source is usually an environmental heat source: air (directly used or indirectly, e.g. preheated by a solar collector) and different ground sources are available. Sewage water is an interesting alternative. The big advantage over compression heat pumps is that the low temperature heat source needed for the same heating duty is only about half the size. Driving heat is provided most commonly by an internal gas burner but can also be provided by other heat sources as e.g. district or waste heat.

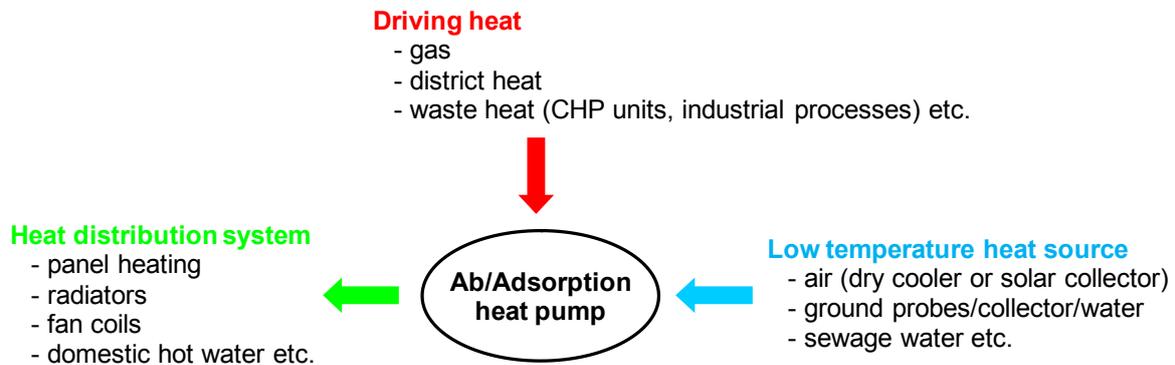


Figure 14: Ab/Absorption heat pump system

For chillers and refrigeration systems the low temperature heat source is the cold distribution system. The low temperature level provided by sorption cooling machines ranges from -40°C for refrigeration purposes or industrial processes to 6 to 18°C for air-conditioning (chilled water). Condensation and absorption heat are usually rejected to the ambient air directly or via a cooling water circuit (dry cooler, wet or hybrid cooling tower) or to the ground (ground probes, ground collector, ground water). The cooling water temperature range is mainly between 23 and 40°C but may also be higher. Driving heat is preferably provided by solar or waste heat (e.g. from combined heat and power units or plants). For reasons of energy efficiency, the use of fossil fuels to drive a sorption chiller should be avoided (Ziegler 2009). The driving heat level required depends on the temperature lift. A high temperature lift requires a high driving temperature. Temperatures from typical driving heat sources range from around 55°C (solar cooling) up to 95°C (district heat). Higher driving temperatures, e.g. from industrial processes or concentrating solar collectors above 120°C allow for the use of advanced cycles, e.g. double-effect.

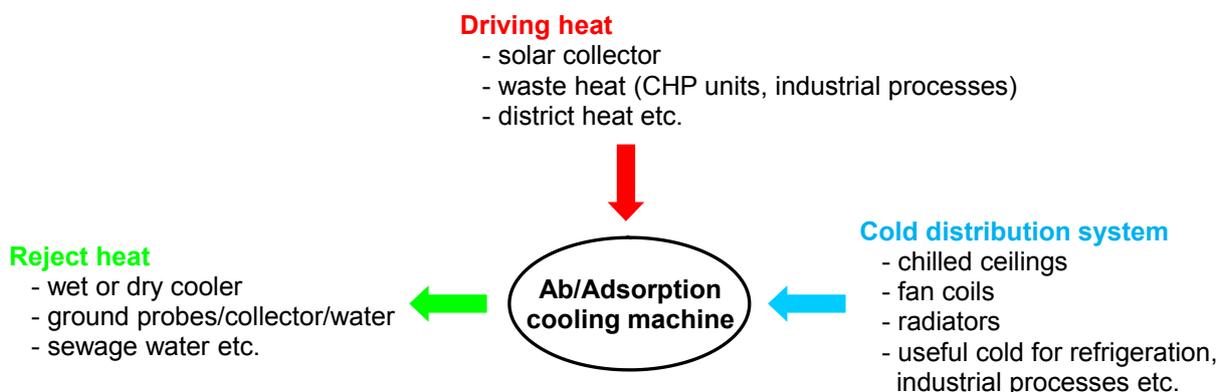


Figure 15: Ab/Absorption cooling system

It is easy to see that the heat pump can be used for heating in winter and cooling in summer when heat sink and low temperature heat source are interchanged. The heat pump can also

be used for simultaneous heating and cooling, e.g. if in heating period server rooms have to be cooled. In this case, efficiency is the highest. However, in most cases cooling and heating demands do not occur at the same time.

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