

# THERMODYNAMIC CYCLE

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The operating principle of a heat pump is based on the physical property that "the boiling point of a fluid increases with pressure". By lowering pressure, a medium can be evaporated while an increase of pressure will lead to condensation.

For large scale industrial applications, Ammonia is the most suitable refrigerant. It is mostly used in a pump system.

## Log P-h diagram

To understand the principle of operation of an mechanical heat pump, a log P-h diagram can be used. A log P-h diagram shows all state variables of the refrigerant. On the horizontal axis enthalpy (h) is shown. The vertical axis has a logarithmic scale and shows pressure. The other lines show:

Red: Temperature [ $^{\circ}\text{C}$ ]

Blue: Entropy [ $\text{kJ/kg}$ ]

Green: Specific volume [ $\text{m}^3/\text{kg}$ ]

The black line divides the graph according to the different states of Ammonia ( $\text{NH}_3$ ). On the left its fluid phase is shown. On the right side Ammonia is in its gaseous state. Below the black curve a combination of both gaseous and liquid Ammonia can be found. The area above the highest point is called the transcritical area.

## The thermodynamic cycle

The log p-h diagram shows a cycle for a mechanical heat pump. The points represent the different components of the heat pump. The condensation temperature of  $80^{\circ}\text{C}$  and an evaporation temperature of  $40^{\circ}\text{C}$  is taken as an example.

**1-2 The compressor:** With a compressor the pressure of the gaseous refrigerant is increased from 15 to 40 bar. Ideally the entropy remains constant, in reality the entropy will increase somewhat, because the electric energy needed to power the compressor is partly absorbed by the refrigerant. The temperature of the  $\text{NH}_3$  gas will rise to  $120^{\circ}\text{C}$ .

**2-3 The condenser:** The condenser delivers useful energy. In the condenser the superheated gas is cooled from  $120^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ , until all vapour has become liquid. The liquid flows to the expansion device.

**3-4 Expansion device:** Inside the expansion device the pressure is reduced from 40 to 15 bar. Due to the expansion a mixture of liquid and gas is formed. This mixture flows to the liquid separator.

**4-5/1 Liquid separator:** Inside the liquid separator both liquid (5) and gaseous (1) Ammonia can be found. Its most important function is to separate the liquid from the gas. The vapour flows to the compressor; the liquid is pumped over the evaporators.

**5-6 Evaporator:** The liquid ammonia at the bottom of the separator is pumped over the evaporator(s). Inside the evaporator the liquid is evaporated at a constant temperature of  $40^{\circ}\text{C}$ . The energy needed for evaporation is delivered by a source of waste heat. The mixture of liquid and gas flows back to the separator (6) and is separated again in liquid and vapour.

## Coefficient of Performance

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The efficiency of refrigeration systems and heat pumps is denoted by its Coefficient Of Performance (COP). The COP is determined by the ratio between energy usage of the compressor and the amount of useful cooling at the evaporator (for a refrigeration installation) or useful heat extracted from the condenser (for a heat pump). A high COP value represents a high efficiency.

Most of the electric energy needed to drive the compressor is released to the refrigerant as heat. Therefore more heat is available at the condenser than is extracted at the evaporator of the heat pump.

For a heat pump a COP value of 4 means that the addition of 1 kW of electric energy is needed to have a release of 4 kW of heat at the condenser. At the evaporator side 3,0-3,5 kW of heat is extracted. The additional heat is generated by the compressor. On the other hand: For a refrigeration system a COP of 4 indicates that 1 kW of electricity is needed for an evaporator to extract 4 kW of heat. Due to this important difference in COP definition, for a heat pump one often speaks of COP<sub>h</sub>. In this abbreviation 'h' means heating.

The efficiency of a heat pump, COP<sub>h</sub>, depends on several factors. Especially the temperature difference between waste heat and the condensation temperature is an important factor. The temperature difference between condensation and evaporation temperature mainly determines the efficiency: the larger the difference, the higher the efficiency. The figure on the left shows the influence of this temperature difference on the COP<sub>h</sub> value. These values are based on figure 10.10 in the book 'Refrigeration and Air Conditioning' by Ammonia. The figure shows an increase in COP<sub>h</sub> with an increasing evaporation temperature. Furthermore it shows a decrease in COP<sub>h</sub> with an increasing condensation temperature. In general the COP<sub>h</sub> decreases with an increase in temperature difference between condensation and evaporation. The figure is an indication of the dependence of the COP<sub>h</sub> of an Ammonia heat pump as a function of this temperature difference.

Another important factor that influences efficiency is the applied [refrigerant](#). Ammonia, for example, is a very efficient refrigerant. At an evaporation temperature of 30 °C and condensation temperature of 70 °C. These same conditions only give a COP<sub>h</sub> of 4,5 for refrigerant R410A. Other factors that influence the efficiency of a heat pump are system controls, efficiency of peripheral equipment like fans, pumps, etc.

## Carnot efficiency

The theoretical maximum efficiency of a heat pump is described by the Carnot-efficiency:

The equation shows that the Carnot-efficiency depends on the condensation and evaporation temperature. With an ideal compressor and condenser/evaporator one can achieve the Carnot efficiency. However, in practice there are a lot of parameters that have a negative influence on the efficiency. The actual efficiency is the product of the Carnot efficiency and the system efficiency:

The system efficiency is usually 50% to 70%.

## Lorentz efficiency

With a [transcritical heat pump](#) the Carnot-efficiency can not be used, because there is no condensation temperature, but a temperature of the gas cooler. The maximum efficiency of a transcritical heat pump is described by the Lorentz efficiency.

T<sub>m</sub> is the mean temperature in the gas cooler. This temperature is calculated from the temperature at the inlet and the outlet of the gas cooler:

Similar to Carnot, the Lorentz efficiency will not be reached in practice due to all kind of losses. To determine the real efficiency, the following losses must be taken into account:

# Refrigerants

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A variety of refrigerants are available for usage in mechanical heat pumps. With each of them having their own advantages and disadvantages the choice of refrigerant depends on several criteria.

## Selection criteria

In general the following criteria must be taken into account:

**Pressure:** At a given temperature the condensation pressure is different for different refrigerants. For certain refrigerants at high temperatures, pressure will become too high and normal heat pump components

can no longer be applied. Low pressure is another risk: for low pressures the volume that needs to be swept increases. This requires larger components and thus an increase in investments. The figure below shows the temperature of evaporation as a function of pressure for several commonly used refrigerants.

At the [download-page](#) physical properties of several commonly used refrigerants can be downloaded.

**Critical temperature:** Above a certain temperature a refrigerant reaches its supercritical area. Within the supercritical range the fluid and gaseous phase of the refrigerant can no longer be distinguished.

**Energy efficiency:** The efficiency of a heat pump depends on the choice of refrigerant.

**Natural versus synthetic refrigerants:** Most synthetic refrigerants (HFC's) contribute strongly to the greenhouse effect in case of leakage. This impact can be 3000 times higher as compared to CO<sub>2</sub>.

Besides the criteria mentioned above, several other factors are also involved in decision making. Investment costs, required size of the installation and safety and permits have to be taken into account when deciding what refrigerant to use.

## Refrigerant tags

All refrigerants are denoted by a code. The code is started by a letter 'R' (Refrigerant) and followed by a number. From this number can be deduced:

**R000-R399:** Chemical refrigerants of which the composition is determined by their code number. General code: Rxyz= R(number of C atoms)(number of H atoms)(number of F atoms). R134, for example, consists of two C atoms, 4 H atoms and 4 F atoms: C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>.

**R400-series:** Zeotrope mixtures of refrigerants that do not have a evaporation point but rather a evaporation range. Evaporation temperature changes during the increase of temperature with a few degrees.

**R500-series:** Azeotrope mixtures with a fixed evaporation point.

**R600-series:** Other organic refrigerants.

**R700-series:** Inorganic refrigerants.

## Refrigerants for heat pumps

Below, several frequently used refrigerants in heat pumps are described.

**R134a** is used as a refrigerant for medium sized or large heat pump systems. As compared to refrigerants R407c and R410a compared to refrigerant NH<sub>3</sub> its efficiency is lower. The pressure in R134 is fairly low. Due to this the volume that needs to be swept is therefore higher investments are needed for installation.

**R407c and R410a** are frequently used in small to medium sized heat pump systems. These refrigerants are regularly used in air conditioning and heating. R410a is supercritical above a temperature of 71 °C. Above this temperature a difference between liquid and gas phase can no longer be made. R410a can be applied in low temperature heat pump systems. As compared to R134a the volume that can be swept is lower. Therefore investment costs. On the other hand: its efficiency as compared to R134a is lower as well.

**R600 (butane) and R600a (isobutane)** are used for refrigeration installations. These refrigerants are also suitable for use in heat pumps with temperatures higher than 80 °C. Many refrigerants give high pressures at these temperature levels. For R600 and R600a the increase in pressure is very high. Because of a fire and explosion hazard, installations with R600 and R600a should meet safety requirements of NPR-7600.

**R717 (Ammonia)** is the most suitable refrigerant for usage in a heat pump in industrial environments. Ammonia has a high efficiency at temperatures of 80 °C. Expectations are that this range will soon be widened up to temperatures of 90 °C. Furthermore, Ammonia does not contribute to the greenhouse effect. Ammonia has been frequently used as a refrigerant in refrigeration systems. The experience with Ammonia to this, can be used when installing heat pumps with Ammonia as a refrigerant. It is inflammable and toxic but due to its high efficiency Ammonia installation should meet the requirements of PGS-13.

**R744 (CO<sub>2</sub>)** is another natural refrigerant. It is used in refrigeration installations, often in combination with Ammonia or R600a. Ammonia in the system. For low temperature freezer applications a system can be built up of CO<sub>2</sub> compressors combined with R600a. The condensation temperature is 31 °C. Above this temperature condensation does not take place at a constant temperature, instead it occurs over a temperature range. Therefore the heat pump can only be applied in situations where a potential user allows for heating at non-constant temperature. It can do function above the supercritical temperature: [CO<sub>2</sub> supercritical heat pumps](#).

**R718 (Water)** can also be used as a refrigerant. Water has the advantages that it is easily obtained and does no damage to the system.

temperatures ( $> 100\text{ }^{\circ}\text{C}$ ). At these temperatures pressures in other refrigerants can become too high. A disadvantage of the state. A relatively high compressor capacity is necessary because to this.

## Mechanical heat pump

The mechanical heat pump is the most prevailing heat pump to be applied commercially. Its principle of operation: Inside a mechanical heat pump the pressure of a refrigerant is increased with the use of a compressor. Due to this increase in pressure, the condensation temperature rises. Most installations have an electric motor to drive the compressor. Two types of mechanical heat pumps are available: a system that with direct expansion of the refrigerant at the inlet of the evaporator (dx system) and a so called 'pump system' heat pump where liquid refrigerant is pumped to the evaporators. Both types are described in more detail below.

### DX-system

The figure on the right shows a system with direct expansion. Direct expansion implies that the entire refrigerant volume at evaporator. Due to the expansion, a large part of the fluid refrigerant evaporates, denoted as flash gas. The refrigerant, liquid and gas, flows back to the compressor. Only the liquid part of the refrigerant has the ability to evaporate in the evaporator. When the refrigerant is to the compressor. The superheating is necessary to prevent the compressor from damage due to liquid slugging. The expansion device, is controlled by the degree of superheating measured at the outlet of the evaporator. The compressor temperature at the compressor outlet.

### Pump

The other type of the mechanical heat pump is the pump system heat pump. The figure on the left shows its principle of operation. From this vessel, fluid refrigerant is pumped to the evaporator(s). Inside the evaporator the refrigerant is partially evaporated. The refrigerant flows back to the separator vessel. This vessel separates the refrigerant in liquid and vapour. The liquid is pumped to the compressor. An advantage of this system is that smaller evaporators can be used as compared to dx systems with the entire refrigerant solely. On the other hand, an additional refrigerant pump and separation vessel are needed. Pump system heat pumps are used in industrial applications. The majority of heat pumps with Ammonia are built as a pump system type. Ammonia dx systems are not used. Besides, overheating of the refrigerant in dx systems causes high discharge temperature.

## Absorption heat pump

Where a mechanical heat pump is driven by electric energy, an absorption heat pump is driven by thermal energy. This thermal heat is delivered by steam or by combustion of natural gas. Absorption heat pumps are very useful in situations where both heating and cooling is required.

The principle of operation of an absorption heat pump is based on absorption and evaporation of a refrigerant. An absorption medium as well as a refrigerant have to be chosen. Well known pairs are:

1. Lithium-bromide (LiBr) and water, in this case water is the refrigerant and LiBr the absorption medium.
2. Ammonia and water, with Ammonia as the refrigerant and water as absorption medium.

### Principle of operation

The figure on the right shows the principle of operation of an absorption heat pump. It is based on a heat pump that uses absorption heat pump consists of two loops. The loop on the right represents the absorption medium and the circulation loop of the refrigerant.

At the intersection of  $P_1/T_2$ , thermal energy is added to the generator of the heat pump. As a result the refrigerant is evaporated.

pressure. The absorption medium is lowered in pressure with the use of an expansion device and flows towards the absorber. The gas is absorbed (intersection  $P_0/T_1$ ). Due to the absorption process, useful heat is released at an intermediate temperature. The pressure is increased by a pump and flows back to the generator. To increase efficiency, an internal heat exchanger is used to preheat the cold mixture.

### Refrigeration

At the intersection of  $P_1/T_2$ , thermal energy is added to the generator of the heat pump. As a result the refrigerant is evaporated at low pressure. The gas flows towards the condenser. Inside the condenser the  $\text{NH}_3$  releases heat to its environment and will condense. The pressure inside an expansion device is lowered and flows towards the evaporator. At low temperature (at intersection point  $P_0/T_0$ ) the refrigerant will evaporate. Waste heat can be used as heat source, but it is also possible to use the evaporator for cooling purposes. The refrigerant is absorbed where it is absorbed in water. Due to the absorption useful heat is released.

## Efficiency

Absorption heat pumps with natural gas as a heat source are commercially available. For the production of useful heat at a rate of 1 kW, the condenser with water or air, the efficiency is approximately 150%. In other words: the addition of 1 kWh of natural gas results in 1.5 kWh of useful heat.

# Adsorption heat pump

The principle of operation of adsorption heat pumps is equal to that of the [absorption heat pump](#). The only difference is that an adsorption heat pump uses solid-sorption instead of the liquid-sorption that is used in absorption systems. The material pairs stated below are regularly applied in adsorption heat pump systems.

Silica gel –  $\text{H}_2\text{O}$

Zeolite –  $\text{H}_2\text{O}$

Active carbon – MeOH

Active carbon/salt -  $\text{NH}_3$

The adsorption principle is more and more used in small heat pump systems (70-500 kW), that are mainly used for cooling.

# Transcritical CO2 heat pump

Above 31 °C,  $\text{CO}_2$  is transcritical. For transcritical  $\text{CO}_2$ , heat intake at the evaporator takes place below the critical pressure of 71 bar. The release of heat within the gas cooler takes place above the critical pressure of 71 bar. Due to this, heat is released over a temperature range. This is in contrast with conventional compressor systems where heat release takes place at a fixed temperature. Therefore we talk about a gas cooler instead of a condenser; the refrigerant will not condensate, it is only cooled. The figure below shows the T-s diagram of a transcritical heat pump cycle with the refrigerant  $\text{CO}_2$ . A waste water flow (orange) is cooled in the evaporator from 28 °C to 23 °C and process water (pink) is heated in the gas cooler from 20 °C to 70 °C. The red lines are lines of constant pressure.

The blue line represents the transcritical heat pump cycle. The steps in the cycle are:

- 1 - 2 Compression to transcritical pressure
- 2 - 3 Gas cooling in transcritical area, to heat process water
- 3 - 4 Expansion to low pressure
- 4 - 5 Evaporation by cooling down the waste water flow
- 5 - 1 Superheating in evaporator

The efficiency of a transcritical

The efficiency of a heat pump is given by a COP. The COP of a heat pump is usually calculated using the evaporation temperature. However, a transcritical heat pump has no condensation temperature, but a temperature range in the gas cooler. To calculate the mean temperature ( $T_m$ ) in this temperature range. This mean temperature is calculated using the temperature at the inlet of the gas cooler and the outlet of the gas cooler (point 3). [Read more about this](#).

#### **Advantages CO<sub>2</sub> transcritical heat pump:**

For a high temperature lift at the side of the gascooler (at least 30-40 °C) and a low temperature of the water that needs to be heated, the CO<sub>2</sub> transcritical heat pump can be higher than conventional heat pumps.

#### **Disadvantages CO<sub>2</sub> transcritical heat pump:**

The temperature of the water that needs to be heated has to be low enough to make an efficient heat pump. When the water flowing in, the process will not be efficient. In this situation an Ammonia heat pump is a better solution.

The system works with high refrigerant pressures of more than 100 bar.

## Hybrid heat pump

Hybrid heat pumps, or compression resorption heat pumps, combine technologies of an absorption and compression heat pump. Hybrid heat pumps use a mixture of media, for example, NH<sub>3</sub> and water. Due to changes in composition of the mixture caused by absorption and desorption, heat is extracted and emitted at a non-constant temperature. This temperature glide may lead to an increase in efficiency.

A hybrid heat pump consists of the following main components:

1. Desorber: in here waste heat is extracted by the mixture from the environment.
2. Separator: the separator separates water and Ammonia.
3. Pump: the pump increases the water pressure.
4. Compressor: Ammonia is compressed to a high pressure inside the compressor.
5. Absorber: in here useful heat is released towards the environment.
6. Expansion element: in here the pressure of the mixture is lowered.

A large temperature glide for absorption and desorption is favourable to decrease the ratio of compression inside a heat pump. As compared to the conventional mechanical heat pump, an equal lift in temperature can be realised with a lower compression ratio when using a hybrid heat pump. As a result a higher COP can be reached. To increase the range of the temperature glide, the sizes of absorber and desorber should be increased as well (making them more expensive). Proper adjustment of the temperature glides and temperature ranges of the heat pump, is therefore essential to maximize efficiency. The use of media that can condensate or evaporate will lower the COP dramatically.

### Advantages of hybrid heat pumps:

The condensation temperature is higher as compared to conventional compression machines. This is due to the saturation pressure of the mixture than for a pure gaseous refrigerant flow.

In connection to what is mentioned above a large temperature lift is possible with a high COP.

### Disadvantages of hybrid heat pumps:

Its technical complexity causes the hybrid heat pump to be expensive to install.

There is a limited number of manufacturers offering hybrid heat pumps.