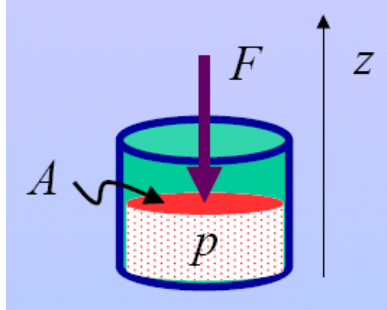


Thermodynamics

Mechanical work

“Work = force x distance”.



If we apply a force dF along a distance dz on a volume V of gas with pressure p and area A in the z -direction, the work done on the gas volume is:

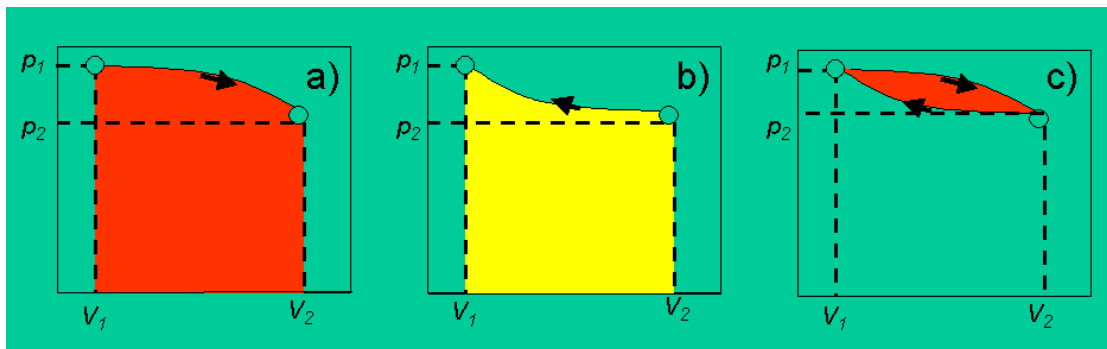
$$dW = - F \cdot dz = - \frac{F}{A} \cdot A \cdot dz = - p \cdot A \cdot dz = - p \cdot dV$$

Note: If the gas is being compressed, the work done is positive, since both dz and dV are negative!

If we take the integral of this expression we obtain:

$$W = - \int_i^f p dV, \text{ where } p = p(V), \text{ i.e. } p \text{ varies with respect to the volume } V.$$

Let us look at a situation where we go from 1 to 2 and back as in the figure below:



a) If we start integrating from 1 to 2 we get: $W_{12} = - \int_1^2 p dV < 0$ (expansion)

b) If we go in the opposite way according to b) we get: $W_{21} = - \int_2^1 p dV > 0$ (compression)

c) If we now go in a cyclic way we get c) $W_{121} = - \int_1^2 p dV - \int_2^1 p dV = W_{12} + W_{21} < 0$

Here we see that the integration has been performed on the encapsulated area. In this example, the work done *on the system* is negative, which means that the work done *by the system* is positive. We have an engine!

Heat

If we have a closed volume V enclosing a gas, and add heat to the gas we often denote it with Q (J). The temperature of the gas changes from T_1 to T_2 or by ΔT according to:

$$Q = cm(T_2 - T_1) = cm\Delta T$$

Sometimes this constant c is denoted c_V to show that the volume is constant. If the pressure instead is kept constant we denote the constant c_P .

The constant c is called the constant of heat capacity. The larger the value the more heat can be stored in the medium.

First law of thermodynamics

This law is just the law of energy conservation. If we have a system (gas, liquid etc) it can have a so-called internal energy U , consisting of kinetic energy of the molecules or energy of the vibrating or rotating molecules. In simple gases, the kinetic energy usually dominates, while in solids the contribution to c mainly comes from the vibrational energy.

In words the law can be written: ***Change in internal energy = Heat supplied to the system + Work done on the system.***

Using formulae we have:

$$\Delta U = \Delta Q + \Delta W$$

Using differentials we get:

$$dU = dQ + dW$$

For systems where chemical reactions occur, e.g. fuel cells, appropriate terms related to the chemical processes can be added to the right hand side of this equation. The terms are related to the *chemical potentials* of the ingredients, and reflect the energetics of the chemical reactions taking place in the system.

In thermodynamics, the chemical potential is usually called *Gibbs free energy*. In order to be able to treat these more complex 'engines', a number of additional terms need to be introduced, one of them being the notion of **entropy**:

Entropy

The Entropy, S , is a variable used in thermodynamics and is a measure of the probability P , of a certain state to occur:

$$S = k \cdot \ln P$$

One often uses another expression for a system to describe the Entropy:

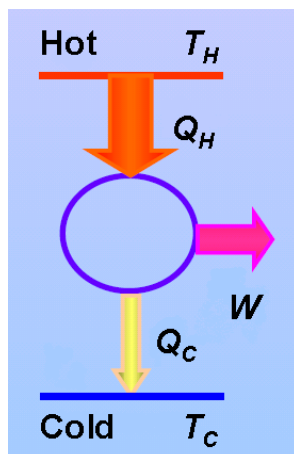
$$dS = \frac{dQ}{T}$$

One also discusses reversible and irreversible processes, where most processes are irreversible in practice. We can never gain energy from only one reservoir; we need two with some temperature difference. This is the principle of all kinds of heat engines, such as turbines based on steam, car engines etc.

If we look at the Universe, we have:

$$dS \geq 0$$

Heat engine



This figure describes how a heat engine works. The heat flows from the hot reservoir towards the cold reservoir thus performing work:

$$W = \Delta Q = Q_H - Q_C$$

The heat Q_H flows from the hot reservoir with temperature T_H , and goes into an apparatus that converts heat to mechanical work W . The apparatus produces a heat loss equal to Q_C at a temperature of T_C . The mechanical work W comes out of the apparatus.

Let us look at the entropy of the whole system and use the equations above:

$$\Delta S = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = -\frac{Q_H}{T_H} + \frac{Q_H - W}{T_C} \geq 0$$

If we now rewrite this equation we get:

$$-\frac{Q_H}{T_H} + \frac{Q_H}{T_C} \geq \frac{W}{T_C} \Rightarrow W \leq Q_H \left(1 - \frac{T_C}{T_H}\right)$$

The *thermal efficiency* is denoted by η and we define $\eta = \frac{\text{useful output}}{\text{required input}}$ and with the formulas:

$$\eta = \frac{W}{Q_H} \leq \left(1 - \frac{T_C}{T_H}\right)$$

The so-called Carnot efficiency $\eta_{Carnot} = 1 - \frac{T_C}{T_H}$ is the maximum efficiency we can

obtain. The factor $\frac{T_C}{T_H}$ is called the *thermodynamic loss*. In some cases the energy

W_{out} is called *Exergy*, useful energy.

Example

Suppose we have a large iceberg with volume 1 km x 1 km x 100 m and temperature 0°C (T_1). Put the density to 1 kg/dm³. It is moving from the North southwards in the Atlantic, where the temperature is 20°C (T_2). Regard the Atlantic as a hot source and the iceberg as a cold sink. Estimate how much work the melting of the iceberg would generate. Compare how long time a power plant of 1000 MW has to work to generate the same energy.

Solution

From tables we know that when one melts a kilogram of ice the heat is around 335 kJ. The melting iceberg thus absorbs $(10^3 \times 10^3 \times 100) \text{ m}^3 \times 10^3 \text{ kg/m}^3 \times 335 \text{ kJ} = 3.35 \times 10^{16} \text{ J}$. With the heat engine rule, the maximum work we can get is

$$W = Q_2 \frac{T_1 - T_2}{T_2} = 3.35 \times 10^{16} \frac{293 - 273}{293} = 3.35 \times 10^{16} \times 0.068 \text{ J} \approx 2.3 \times 10^{15} \text{ J}$$

$$t = \frac{W}{P} = \frac{2.3 \times 10^{15}}{1000 \times 10^6 \times 3600 \times 24} \text{ days} = 27 \text{ days}$$

So it is around month's work for such a large power plant.

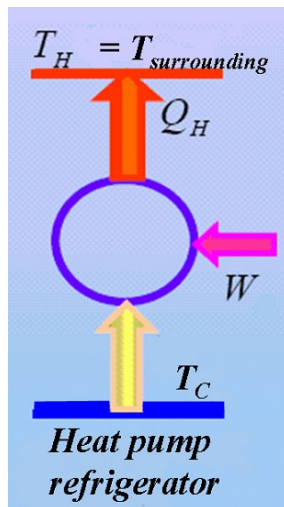
Coefficient of Performance, COP

In the expression $\frac{W}{Q_H} \leq \left(1 - \frac{T_C}{T_H}\right)$

we define the coefficient of performance; *COP*, as:

$$COP = \frac{W}{Q_H} \text{ for instance when we discuss refrigerators.}$$

Refrigerator. Heat pump



The above picture describes both the *heat pump* and the *refrigerator*. The 4:th year KTH students, Baltzar von Platen and Carl Munters invented the absorption refrigerator in 1922. It became a worldwide success and was commercialized by Electrolux in Stockholm.

Heat is taken from a low temperature reservoir, work is put in and heat is added to the high temperature reservoir.

In this section we denote coefficient of performance, *COP*, and it is defined as:

$$COP = \frac{\text{useful output}}{\text{required input}} = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} = 1 / \left(\frac{Q_H}{Q_C} - 1 \right)$$

One can rewrite this formula in terms of temperature instead, since in a cycle the total entropy $\Delta S \geq 0$ and we find

$$- \frac{Q_C}{T_C} + \frac{Q_H}{T_H} \geq 0, \text{ making it possible to change the } COP \text{ number as a function of}$$

temperatures:

$$COP \leq 1 / \left(\frac{T_H}{T_C} - 1 \right). \text{ The equality sign holds when there is no net increase in entropy.}$$

Example

Let us look at a normal refrigerator in the household, where $T_H = 273 + 25$ K and $T_C = 273 - 4$ K. What is the *COP* number?

Solution

$$COP \leq 1 / \left(\frac{T_H}{T_C} - 1 \right) = 1 / \left(\frac{298}{269} - 1 \right) = 9.3$$

So, we have $COP \leq 10$

Example

We have a refrigerator operation between the reservoirs at 0°C and 100°C. Let 1.0 kJ of heat be absorbed from the cold reservoir. How many joules will be extracted from the hot reservoir?

Solution

We use the expression $\frac{W}{Q_H} \leq \left(1 - \frac{T_C}{T_H}\right)$ and solve the equation for W :

$$W = 1.0 \times 10^3 \left(1 - \frac{273}{373}\right) J = 268 J \approx 270 J$$

Example

Determine the coefficient of performance, COP , for the refrigerator above.

Solution

The definition for the coefficient of performance is $COP = \frac{W}{Q_H} = \frac{1.0 \times 10^3}{268} \approx 3.7$

Heat pump

The picture above can be used for both a refrigerator and a heat pump. The idea is to get heat inside a house and to put the cold reservoir outside the house. Some heat pumps work with the reservoir as the air around us, while others use ground source heat, which has about the same temperature the whole year. The COP can be found around 3.5-4.0 in such apparatus. The COP definition for a heat pump in steady-state operation is given by:

$$COP = \frac{Q_C}{W} \leq \frac{T_H}{T_H - T_C} = \frac{1}{\eta}$$

Here W stands for the compressor's dissipated work, and η for the efficiency of the so-called Carnot cycle.

In many heat pumps one uses both the evaporation and condensation processes, where one in the system has a special fluid as a refrigerant. The fluid can be evaporated and exist in a gaseous state. One applies a compressor that increases the pressure of the gas and then lets it circulate. The hot pressurized gas is being cooled in a heat exchanger or a condenser, making the gas condense at a high pressure into a liquid that is then evaporated into a gas via absorption of heat. Then the medium returns to the compressor and the cycle repeats itself.

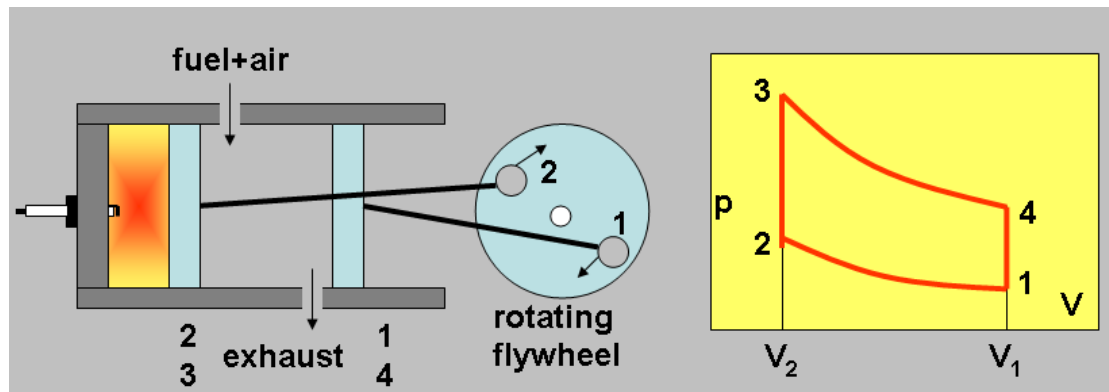
A detailed description of the heat pump is given in a laboration:

http://kurslab.physics.kth.se/klab/Labpek/Heat_pump.pdf

Combustion.

The Otto motor (ordinary car engine)

A combustion engine such as the Otto motor needs fuel (petrol, gasoline, diesel, ethanol) to be mixed with air inside the engine. If we compare with heat engines there is no external heat reservoir included. Below is show how the Otto engine works schematically.



The piston moves inward from position 1 and the fuel/air mixture enters the chamber. When the piston passes the entrance of the fuel/air input, the gas mixture is compressed. One sees on the left figure how the pressure increases. At the end position 2/3 the ignition takes place via the spark plug, the temperature rises and the gas expands from volume V_2 to V_1 . The gas delivers power to the piston that moves to the other end position, and the cycle starts all over again. The efficiency of the Otto motor is rather low and can be expressed by the following equation:

$$\eta = \frac{W}{Q_H} = 1 - \frac{1}{r^{\gamma-1}}$$

The constant r is just the ratio of the two volumes V_1 and V_2 :

$$r = \frac{V_1}{V_2}$$

It is also denoted *compression ratio* and in many engines it is around 8:1. In the formula one also sees the constant γ , which just is

$\gamma = \frac{c_P}{c_V} = 1.4$ for air that can be found in Chemical tables. Thus we have the following formula for the Otto motor:

$$\eta = \frac{W}{Q_H} = 1 - \frac{1}{r^{0.4}}$$

Maximum ratio in the Otto motor is around 10, while in the diesel engine one can reach values up to 25, due to so called self ignition, making the diesel engine much more efficient than the Otto motor.

For an Otto motor the real efficiency is around 30% due to friction losses and that the equations above just holds for ideal gases.

Example

Calculate the maximum efficiency for an Otto motor with compression ratio 8:1.

Solution

$$\eta = \frac{W}{Q_H} = 1 - \frac{1}{r^{0.4}} = 1 - \left(\frac{1}{8}\right)^{0.4} \approx 56\%$$

Steam generator

For such a device where Q_H has a large value the same expression for the efficiency holds:

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

Energy storage

It is not just the efficiency of a system that matters, but only how effectively the different forms can be transferred, e.g. in converting chemical energy to electric energy etc. Below is shown a table where the energy density [kJ/kg] is given for different fuels and storage media.

Deuterium (D-D fusion)	3.3 x 10¹¹
Uranium-235 (fission)	7.0 x 10¹⁰
Hydrogen LHV	1.2 x 10⁵
Methane	6.0 x 10⁴
Gasoline	4.4 x 10⁴
Waterfall fall 100m	9.8 x 10²
Silver oxide-zinc battery	435
Lead acid battery	120