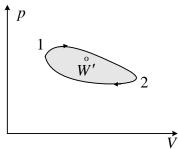
3.7 Cyclic process

A cyclic process is a sequence of processes that leaves the system in the same state in which it started



When a system is carried through a cyclic process its initial and final internal energies are equal. So the total internal-energy change in any cyclic process is zero. Apply the first law for a cyclic process:

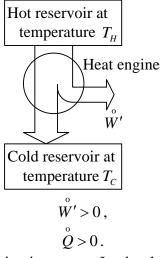
$$\Delta E = Q + W$$

$$\Delta E = 0,$$

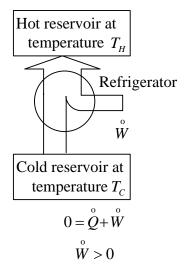
$$\Delta W' = Q.$$

The work done by the system in a cyclic transformation is equal to the heat absorbed by the system.

Heat engine: Any device for transforming heat into work or mechanical energy is called heat engine. All the heat engines absorb heat from a source at a relatively high temperature called hot reservoir, perform some mechanical work, and discard some heat at a lower temperature called the cold reservoir. The schematic diagram of a heat engine is shown on the figure:

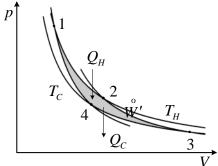


Refrigerator is a heat engine operating in reserve. It takes heat from a cold place and gives off heat to a hot place and requires a net input of mechanical work. The schematic diagram of the refrigerator shows, the heat leaving the system and given to the hot reservoir is greater then taken form the cold reservoir.



3.7.1 The Carnot Cycle

The most important cycle is called Carnot cycle. This consists of two isothermal and two adiabatic processes. Suppose that the working substance is an ideal gas.



The four processes are:

1. The gas expands isothermally at temperature T_H absorbing heat Q_H ,

$$Q_H = nRT_H \ln \frac{V_2}{V_1} > 0.$$

- 2. It expands adiabatically until its temperature drops to T_c .
- 3. It is compressed isothermally at $T_{\rm C}$, rejecting heat $Q_{\rm C}$,

$$Q_C = nRT_C \ln \frac{V_4}{V_3} < 0$$
.

4. It is compressed adiabatically back to its initial state at temperature T_H .

We define the thermal efficiency of an engine as:

$$e = \frac{\stackrel{\circ}{W}'}{Q_{\scriptscriptstyle H}},$$

where Q_H is the absorbing heat, and $\stackrel{\circ}{W}$ ' is the work done by the system in a cycle. We have already seen, that the work done by the system in a cyclic transformation is equal to the heat absorbed by the system.

$$\overset{\circ}{W}' = \overset{\circ}{Q},$$

In this situation:

$$\overset{\circ}{Q} = Q_H + Q_C,$$

therefore:

$$e = \frac{Q_H + Q_C}{Q_H} = 1 + \frac{Q_C}{Q_H}.$$

$$\frac{Q_C}{Q_H} = \frac{T_C \ln \frac{V_4}{V_3}}{T_H \ln \frac{V_2}{V_1}}.$$

Due to the Poisson equation:

$$\begin{split} T_H V_1^{\kappa-1} &= T_C V_4^{\kappa-1} \\ T_H V_2^{\kappa-1} &= T_C V_3^{\kappa-1} \\ \frac{V_1}{V_2} &= \frac{V_4}{V_3} \,, \end{split}$$

SO

$$\frac{V_4}{V_3} = \left(\frac{V_2}{V_1}\right)^{-1}$$

and

$$\frac{Q_C}{Q_H} = \frac{T_C \ln\left(\frac{V_2}{V_1}\right)^{-1}}{T_H \ln\frac{V_2}{V_1}} = -\frac{T_C}{T_H},$$

$$e = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H}.$$

This surprisingly simple result says that the efficiency of a Carnot engine depends only on the temperatures of the two heat reservoirs. The Carnot engine has the maximum efficiency operating between the same two temperatures.

3.8 Cyclic processes in combustion engines

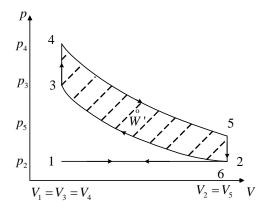
The most wide-spread heat engines are the so called internal combustion engines. Most cars are powered by these engines. In these engines the heat is produced combustion or explosion of gas mixture in the cylinder. The gas mixture is produced by the carburettor.

The hot exhaust pushes a piston which is connected to a crank-shaft to produce power. The burning of fuel is not continuous process, but occurs very quickly at regular time intervals. Between ignitions the engine parts move in a repeated sequence called cycle. The engine is called four stroke engine, because there are four movements or strokes of the piston during one cycle.

3.8.1 Ideal Otto thermodynamic cycle

Now we discuss the ideal Otto thermodynamic cycle. There are two main parts to engine operation. The mechanical operation of the engine, and the thermodynamic processes through which the engine produces work and power.

During the cyclic process, the system gains heat at a constant volume process and gives off heat also along a constant volume process, and they are connected by two adiabatic processes. In the case of adiabatic process there is no heat transfer either into or out of the system. The next figure shows the p-V diagram of the ideal Otto cycle.



The strokes of an ideal four stroke engine:

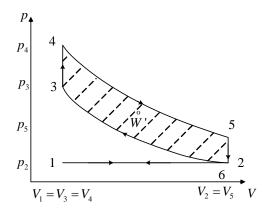
1. intake stroke $1 \rightarrow 2$ 2. compression stroke $2 \rightarrow 3$ 3. power stroke $4 \rightarrow 5$ 4. exhaust stroke $6 \rightarrow 1$

Consider now the different processes. In state 1. the pressure is near atmospheric pressure and the gas volume is at a minimum. During the $1 \rightarrow 2$ process the piston is pulled out of the cylinder with the intake valve open. The pressure remains constant and the volume increases as the fuel/air mixture is drawn into the cylinder form carburettor. In process $2 \rightarrow 3$ the piston moves back into the cylinder with closed intake valve and compresses the fuel mixture adiabatically. The volume decreases and the pressure increases, work is done on the gas by the piston. $3 \rightarrow 4$ is the combustion process of the fuel/air mixture. The combustion is very fast and the volume remains constant. The heat released during combustion increases both the temperature and pressure. $4 \rightarrow 5$ the adiabatically expanding gas do work on the piston and is driven toward the crank-shaft. At the state 5, the exhaust valve is opened and the residual heat in the gas is exchanged with the surroundings. The volume remains constant and the pressure drops to atmospheric pressure. During process $6 \rightarrow 1$ the piston moves back into the cylinder and drives out burned gases at open exhaust valve. At state 1, exhaust valve closes and intake valve opens, and the cycle repeats itself.

The work done by the system W' is equal to the enclosed area. The work times the rate of the cycle (cycles per second) is equal to the power produced by the engine.

Write now the equations of the different thermodynamic processes, but first denote the different values of the temperature, volume and pressure on the p-V diagram. Consider now the cyclic process only.

$$2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 2 \dots$$



For the adiabatic compression $2 \rightarrow 3$ we can apply the so called Possion equations.

$$p_2 V_2^{\gamma} = p_3 V_3^{\gamma}, \qquad \left(\frac{V_2}{V_3}\right)^{\gamma} = \frac{p_3}{p_2}.$$

We call the ratio of the volume at the beginning of compression to the volume at the end of compression the compression ratio denoted by r, and so:

$$\frac{p_3}{p_2} = r^{\gamma} .$$

A other Poisson equation between volume and temperature:

$$T_2 V_2^{\gamma - 1} = T_3 V_3^{\gamma - 1}$$

$$\left(\frac{V_2}{V_3}\right)^{\gamma - 1} = \frac{T_3}{T_2} \to r^{\gamma - 1} = \frac{T_3}{T_2}.$$

 γ is the so called adiabatic exponent:

$$\gamma = \frac{c_p}{c_v} = \frac{f+2}{f}$$

During the combustion process $3 \rightarrow 4$ the volume is held constant and heat is released. If the heat released by unit mass during combustion of fuel denoted by L and use k for fuel/air ratio, m is the mass of the mixture. The heat released:

$$Q_{34} = Lkm$$
,

The change of temperature during this constant volume process:

$$Q_{34} = c_{\nu} m (T_4 - T_3)$$

From the finel temperature we can calculate the final pressure:

$$\frac{p_3}{p_3} = \frac{p_4}{p_4} \to p_4 = \frac{T_4}{T_3} p_3.$$

At the same time p_4 is the pressure at the beginning of the adiabatic expansion. Apply again the Poisson equation for the adiabatic expansion $4 \rightarrow 5$

$$p_4 V_3^{\gamma} = p_5 V_2^{\gamma} \rightarrow \frac{p_4}{p_5} = \left(\frac{V_2}{V_3}\right)^{\gamma} \rightarrow \frac{p_4}{p_5} = r^{\gamma},$$

$$T_4V_3^{\gamma-1} = T_5V_2^{\gamma-1} \longrightarrow \frac{T_4}{T_5} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \longrightarrow \frac{T_4}{T_5} = r^{\gamma-1}.$$

During the cycle
$$Q_{23}=0,$$
 (heat in) $Q_{34}=c_V m(T_4-T_3)>0$ $Q_{45}=0$ (heat out) $Q_{52}=c_V m(T_2-T_5)<0$

The work done by the gas:

We can obtain the power produced by the engine if we multiply the work done by the gas during one cycle with the number of cycles per second denoted by cps.

$$P = \overset{\circ}{W} \cdot cps$$

Calculate now the efficiency of the ideal Otto cycle

$$e = \frac{\stackrel{\circ}{W}'}{Q_{in}} = \frac{c_{s}m (T_{4} - T_{3} + T_{2} - T_{5})}{c_{s}m (T_{4} - T_{3})}$$

$$e = 1 + \frac{T_{2} - T_{5}}{T_{4} - T_{3}} = 1 - \frac{T_{5} - T_{2}}{T_{4} - T_{3}}.$$

Apply the previous equations:

$$\frac{T_3}{T_2} = r^{\gamma - 1}, \quad \frac{T_4}{T_5} = r^{\gamma - 1}$$

$$\frac{T_3}{T_2} = \frac{T_4}{T_5} \to \frac{T_3}{T_4} = \frac{T_2}{T_5}.$$

$$1 - \frac{T_3}{T_4} = 1 - \frac{T_2}{T_5} \to \frac{T_4 - T_3}{T_4} = \frac{T_5 - T_2}{T_5}$$

$$\frac{T_5 - T_2}{T_4 - T_3} = \frac{T_5}{T_4} = \frac{1}{r^{\gamma - 1}}.$$

Finally the efficiency:

$$e = 1 - \frac{T_5}{T_4}$$
, or $e = 1 - \frac{1}{r^{\gamma - 1}}$

During this Otto cycle the maxim temperature is T_4 and the minimum is T_2 , the possible Carnot cycle efficiency

$$e_{carnot} = \frac{T_H - T_C}{T_H} = \frac{T_4 - T_2}{T_4}$$

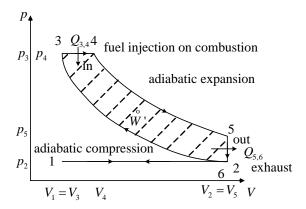
The Otto Cycle efficiency is less than this be cause $T_5 > T_2$.

Now we discussed an ideal Otto cycle, in which there is no heat entering or leaving the gas during the compression and power strokes (they were adiabatical change of states), no friction losses, and instantaneous burning occurring at constant volume. In reality, the ideal cycle does not occur and there are many losses associated with each processes. These losses are normally accounted for by efficiency factors which multiply and modify the ideal result. For a real cycle, the shape of the p-V diagram is similar to the ideal, but the area (work) is always less than the ideal value.

3.8.2 The Diesel Engine

The diesel internal combustion engine differs from the gasoline powered Otto cycle by using a higher compression of the fuel to ignite the fuel rather than using a spark plug, it is compression ignition rather than spark ignition. In the diesel engine, pure air is compressed adiabatically with a compression ratio between 15 and 20. This compression raises the temperature to the ignition temperature of the fuel mixture which is formed by infecting fuel once the air is compressed.

The adiabatic compression followed by a constant pressure combustion process, then an adiabatic expansion as a power stroke and finally an isochoric exhaust. A new air charge is taken in at the end of the exhaust. See on the p-V diagram:



Since the compression and power strokes of this idealized cycle are adiabatic, the efficiency can be calculated from the constant pressure and constant volume processes. During the cycle:

$$Q_{23} = 0,$$
(heat in)
$$Q_{34} = c_p m (T_4 - T_3) > 0$$

$$Q_{45} = 0$$
(heat out)
$$Q_{56} = c_V m (T_2 - T_5) < 0$$

The work done by the gas:

$$\begin{split} \overset{\circ}{W}' &= \overset{\circ}{Q} \\ \overset{\circ}{W}' &= c_p m \big(T_4 - T_3 \big) + c_V m \big(T_2 - T_5 \big) \end{split}$$

The efficiency is:

$$e = \frac{\overset{\circ}{W'}}{Q_{in}} = \frac{c_p m (T_4 - T_3) + c_V m (T_2 - T_5)}{c_p m (T_4 - T_3)} = 1 + \frac{c_V (T_2 - T_5)}{c_p (T_4 - T_3)}$$

It is convenient to express the efficiency in terms of the compression ratio $r_C = \frac{V_2}{V_3}$, and the expansion ratio $r_E = \frac{V_2}{V_4}$, and with the adiabatic exponent $\gamma = \frac{c_p}{c_V}$.

Apply the ideal gas state equation for the different states:

$$pV = nRT$$

$$e = 1 + \frac{1}{\gamma} \cdot \frac{\left(p_2 V_2 - p_5 V_2\right)}{\left(p_3 V_4 - p_3 V_3\right)} = 1 + \frac{1}{\gamma} \cdot \frac{V_2 \left(p_2 - p_5\right)}{p_3 \left(V_4 - V_3\right)} / : V_2 p_3$$

$$e = 1 + \frac{1}{\gamma} \cdot \frac{\left(\frac{p_2}{p_3} - \frac{p_5}{p_3}\right)}{\left(\frac{V_4}{V_2} - \frac{V_3}{V_2}\right)} = 1 + \frac{1}{\gamma} \cdot \frac{r_C^{-\gamma} - r_E^{-\gamma}}{r_E^{-1} - r_C^{-1}}$$

We used the Poisson equations for the adiabatic compression:

$$p_2 V_2^{\gamma} = p_3 V_3^{\gamma}$$

$$\frac{p_2}{p_3} = \left(\frac{V_3}{V_2}\right)^{\gamma} \Rightarrow \frac{p_2}{p_3} = r_C^{-\gamma},$$

and for the adiabatic expansion:

$$p_3 V_4^{\gamma} = p_5 V_5^{\gamma}$$

$$\left(\frac{V_4}{V_2}\right)^{\gamma} = \frac{p_5}{p_3} \Rightarrow \frac{p_5}{p_3} = r_E^{-\gamma}.$$

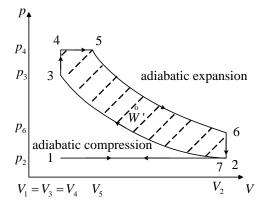
The final formula for the efficiency:

$$e = 1 - \frac{1}{\gamma} \cdot \frac{r_E^{-\gamma} - r_C^{-\gamma}}{r_E^{-1} - r_C^{-1}}$$

For an ideal diesel engine with $\gamma = 1.4$, compression ratio $r_C = 15$ and expansion ratio $r_E = 5$, this gives an ideal diesel efficiency of 56 %.

Rudolf Diesel patented the compression – ignition cycle which bears his name in the 1890s.

The behaviour of many reciprocating engines (engine in which piston moves backwards and forwards inside a glinder) is more adequately represented by the mixed cycle. In this cycle part of heat addition occurs during a constant volume process and the remainder during a constant pressure process (see p-V diagram).



Using the notations:

$$r_C = \frac{V_2}{V_3}$$
, $r = \frac{V_5}{V_4}$ and $r_p = \frac{p_4}{p_2}$

it is possible to show that the efficiency is given by:

$$e = 1 - \frac{1}{r_c^{\gamma - 1}} \cdot \frac{r_p r^{\gamma} - 1}{\left(r_p - 1\right) + \gamma r_p \left(r - 1\right)}$$

3.9 Speed distribution of the molecules in a gas

In a gas all molecular velocities are possible. The molecular speed distribution was originally derived by Maxwell for ideal gas. This formula is called Maxwell's speed distribution law:

$$n(v) = 4\pi N \left(\frac{m_0}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{m_0 v^2}{2kT}}$$

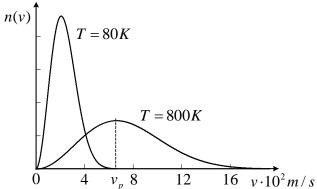
as

$$n(v) = \frac{dn}{dv}$$

so

$$dn = n(v)dv$$

This formula gives the number dn of molecules moving with a speed between v and v + dv, irrespective of the direction of motion. T is the absolute temperature, k is the Boltzmann constant, m_0 is the mass of a molecule, N is the number of molecules. The molecular velocity distribution for oxygen at two temperatures (80 K and 800 K) is shown in the figure:



The peak of the curve represents the most probable speed for the corresponding temperature. v_p can be obtained from the next equation:

$$\frac{dn}{dv} = 0$$
.

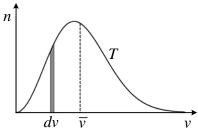
The distribution curve is not symmetrical about the most probable speed. Without proof:

$$v_p = \sqrt{\frac{2kT}{m}} .$$

The average speed is defined as:

$$\overline{v} = \frac{1}{N} \int_{0}^{\infty} n(v) v dv,$$

and it is called the centre of the distribution. Due to the asymmetry it is a bit larger than the most probable value. The shown area on the next figure is just the number of molecules, whose speed is between v and v + dv.



Without proof:

$$\overline{v} = \sqrt{\frac{8kT}{\pi m_0}} \ .$$

Also the integral of the quantity $v^2n(v)$ over all v must equal the average value of v^2 , and its square root is called root-mean-square speed denoted by:

$$v_{rms} = \sqrt{\overline{v^2}},$$

$$v_{rms} = \sqrt{\frac{1}{N} \int_{0}^{\infty} n(v) v^2 dv}.$$

This root-mean-square speed as we have already seen:

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m_0}} .$$

Remark: We find the total number of molecules by integrating the distribution function form zero to infinity with respect to the speed:

$$N = \int_{0}^{\infty} n(v) dv.$$

3.10 Thermal expansion

Most solid materials expand when heated. Suppose a rod of material has a length L_0 at some initial temperature T_0 . When the temperature increases by an amount ΔT , the length increases by ΔL . Experiment shows that if ΔT is not too large, ΔL is directly proportional to ΔT and to L_0 . The proportionality constant α (which is different for different materials) is called the temperature coefficient of linear expansion.

$$\begin{split} \Delta L &= \alpha L_0 \Delta T \ , \\ L &= L_0 + \Delta L = L_0 + \alpha L_0 \Delta T \ , \\ L &= L_0 \left(1 + \alpha \Delta T \right) . \end{split}$$

The unit of α is:

$$\left[\alpha\right] = \frac{1}{K} = \frac{1}{{}^{o}C}$$

In case of metals α is in the order of $10^{-5} \frac{1}{K}$.

The relation above is approximately correct for sufficiently small temperature changes. When the characteristics of a body do not depend on the direction, then the body is called isotropic.

In case of isotropic bodies ΔA the change in area is proportional to the change in temperature ΔT . If $A_0 = ab$, then:

$$A = A_0 + \Delta A = a(1 + \alpha \Delta T)b(1 + \alpha \Delta T),$$

$$A_0 + \Delta A = ab(1 + 2\alpha \Delta T + \alpha^2 \Delta T^2),$$

$$A_0 + \Delta A = A_0 + A_0(2\alpha \Delta T + \alpha^2 \Delta T^2),$$

$$\Delta A = A_0(2\alpha \Delta T + \alpha^2 \Delta T^2).$$

Because $\alpha \Delta T \ll 1$, so $\alpha^2 \Delta T^2 \ll \alpha \Delta T$, that is the second term is negligible:

$$\Delta A = A_0 2\alpha \Delta T$$

In case of isotopic solids the experiments show that if the temperature change ΔT is not too great, the increase in volume ΔV is approximately proportional to the temperature change. The proportionality constant β , which characterizes the volume expansion properties of a particular material, is called the temperature coefficient of volume expansion.

$$\Delta V = \beta V_0 \Delta T \; ,$$

$$V = V_0 + \Delta V = V_0 \left(1 + \beta \Delta T \right)$$

The volume expansion coefficient for a solid material is related to the linear expansion coefficient. To obtain the relation, consider a solid block with dimensions of a, b and c. The original volume is:

$$\begin{split} V_0 &= a \cdot b \cdot c \\ V_0 + \Delta V &= a \left(1 + \alpha \Delta T \right) b \left(1 + \alpha \Delta T \right) c \left(1 + \alpha \Delta T \right), \\ V_0 + \Delta V &= a b c \left(1 + 3 \alpha \Delta T + 3 \alpha^2 \Delta T^2 + \alpha^3 \Delta T^3 \right), \\ \Delta V &= V_0 \left(3 \alpha \Delta T + 3 \alpha^2 \Delta T^2 + \alpha^3 \Delta T^3 \right). \end{split}$$

If ΔT is small the terms containing ΔT^2 or ΔT^3 may be neglected $\alpha^3 \Delta T^3 \ll 3\alpha \Delta T$ and $3\alpha^2 \Delta T^2 \ll 3\alpha \Delta T$.

$$\Delta V = V_0 3\alpha \Delta T$$
,

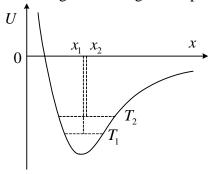
we obtain:

$$\beta = 3\alpha$$
.

Because the shape of a liquid is not definite, only the change in volume with temperature is significant. For liquids β is about ten times greater than that of solids.

3.10.1 An atomic model of thermal expansion of a solid

Model of a crystalline solid: an assembly of atoms held together in a regular three dimensional cubic lattice by a system of spring-like inter-atomic forces. The forces between neighbouring particles in a crystal may be visualized by imagining every particle to be connected to its neighbours by springs. In case of cubic crystal, all springs are assumed to have the same spring constant. Anisotropy is associated with differing spring constants in different directions. At any given temperature the atoms vibrate about their equilibrium position, the higher the temperature the greater being the amplitude of vibration.



Consider only one dimension. Suppose that x represents the distance between two nearest neighbour atoms in lattice. The figure shows the potential energy function U(x) associated with the inter-atomic force. At temperature T_1 the particle can oscillate between two limits whose mid point is x_1 . This is just the average lattice spacing at temperature T_1 . Because of the asymmetry of the potential energy curve at a higher T_2 temperature the amplitude of the oscillation being greater and the mid point is shifted to a greater distance. Thus we see that when the temperature is increased the average distance between atoms increases, which leads to an expansion of the whole solid body.

3.11 Heat transfer

The heat flow or heat transfer is an energy transfer that takes places because of a temperature difference. There are three ways of heat transfer: conduction, convection, and radiation.

3.11.1 Conduction

The transfer of energy arising from the temperature difference between adjacent parts of a body is called heat conduction. If we place one end of a metal rod in a flame and hold the other end, this end gets hotter and hotter, even though it is not in direct contact with the flame. Consider a slab of material of cross-sectional area A and thickness Δx , whose faces are kept at different temperatures. Measure the heat ΔQ that flows perpendicular to the faces in time Δt . Experiments show that the rate of flow of heat through the slab is proportional to the area A, proportional to the temperature difference ΔT and inversely proportional to Δx . That is:

$$\frac{\Delta Q}{\Delta t} \sim A \frac{\Delta T}{\Delta x}$$
.

In the limit of a slab of infinitesimal thickness dx across which there is a temperature difference dT we obtain the fundamental law of heat conduction in which the heat flow rate H is given by:

$$\frac{dQ}{dt} = H = -kA\frac{dT}{dx}$$
.

H is the time rate of heat transfer across the area A. The quantity $\frac{dT}{dx}$ is called temperature

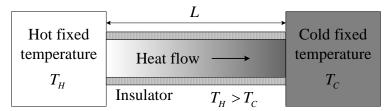
gradient. k is the thermal conductivity, its numerical value depends on the material of the slab. Taking a unit cross-sectional area:

$$h = -k\nabla T$$

Here h is the heat flow rate through unit cross sectional area (heat current density). The heat current density is proportional to the temperature gradient.

This linear connection is not true strictly, because the value of k slightly depends on the temperature, but can be taken to be practically constant if the temperature difference between two parts of the slab is not too great.

Let us apply this law to a rod of length *L* and constant cross-sectional area *A* in which a steady state has been reached. In a steady state the temperature at each point is constant in time.



$$H = -kA\frac{dT}{dx},$$

but for a constant A and k the temperature gradient $\frac{dT}{dx}$ is the same at all cross sections.

Hence, T decreases linearly along the rod so that:

$$-\frac{dT}{dx} = \frac{T_H - T_C}{L}$$
, and $H = kA \frac{T_H - T_C}{L}$.

For thermal insulation in buildings, engineers use the concept of thermal resistance denoted by R. The thermal resistance R of a slab of material with thickness L is defined to be:

$$R=\frac{L}{k}$$
,

using this concept, the heat flow rate:

$$H = \frac{A(T_H - T_C)}{R},$$

or expressed with the heat current density:

$$h = \frac{T_H - T_C}{R} \ .$$

That is the heat current density is equal to the temperature drops divided by thermal resistance. This simple expression makes the calculation of isolation very easy in case of several layers.

Consider a compound slab, consisting of *n* layers having different thermal resistances. In steady state the heat flow rate is the same so:

$$h = \frac{\Delta T_1}{R_1} = \frac{\Delta T_2}{R_2} = \dots = \frac{\Delta T_n}{R_n}$$

Take the sum of all equations:

$$\sum_{i=1}^n \Delta T_i = \sum_{i=1}^n h R_i ,$$

$$\sum_{i=1}^n \Delta T_i = h \sum_{i=1}^n R_i .$$

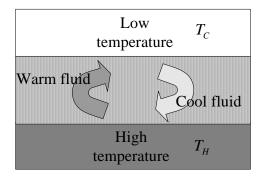
Finally the heat current density:

$$h = \frac{\sum_{i=1}^{n} \Delta T_i}{\sum_{i=1}^{n} R_i}.$$

In addition to conduction, convection and radiation are important processes by which heat is transferred.

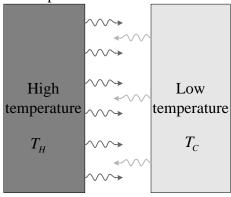
3.11.2 Convection

Convection is when the heat flow is associated with mass flow. In the example the warm fluid rises due to buoyant force and its place is taken by cooler fluid. On the figure there is convection between objects at different temperatures.



3.11.3 Radiation

Radiation is when the heat is transferred by electromagnetic radiation. All object radiate electromagnetic radiation. The amount and character of the radiation is determined by the temperature and surface of the object. In general, the rate of energy emission increases with the fourth power of the absolute temperature.



In the above case there is a net effect due to radiation, and energy is transferred from the warmer object to the cooler object. Since electromagnetic radiation travels through empty space, the radiation does not require physical contact for the transfer of energy.

3.12 Reversible and Irreversible Processes

Quasi-static processes:

Processes in which the system passes through a continuous sequence of equilibrium states are said to be quasi-static. In a quasi-static process the change of the variation is so slow that there is enough time for the thermodynamic variables to take a new value but it is the same at all point of the system. Only quasi-static processes can be plotted with a continuous line on the *p-V* diagram, and they are ideal processes.

Reversible processes are that satisfy the following conditions:

- (a) it can be carried out with equal ease in two opposite direction,
- (b) in each case the system passes through the same intermediate states,
- (c) after carrying out the direct and reverse processes, the system and the surrounding return to their initial states.

Any process which does not satisfy even one of these conditions is irreversible. It can be shown that all quasi-static processes are reversible processes. The reversible processes are only idealisations. There are no strictly quasi-static processes in nature, because all thermal

processes takes place at a finite rate and not infinitely slowly. All real processes in nature are irreversible.

Reversible Cycle:

A cyclic process is a sequence of processes such that the system returns to its original equilibrium state. If the processes involved are all reversible, we call it a reversible cycle. An important reversible cycle is the Carnot cycle discussed earlier.

We defined the efficiency e of a heat engine as the ration of the net work done by the engine during one cycle to the heat taken form the high temperature reservoir.

$$e = \frac{W'}{Q_H}$$

In case of Carnot cycle we have got the next result:

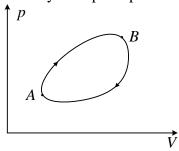
$$e = 1 + \frac{Q_C}{Q_H}$$
, or $e = 1 - \frac{T_C}{T_H}$.

It means that:

$$1 + \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H},$$
$$\frac{Q_C}{T_C} + \frac{Q_H}{T_H} = 0.$$

This equation states that the algebraic sum of quantities $\frac{Q}{T}$ for a Carnot cycle is zero.

As a next step, we state that any reversible cycle is equivalent – to as close an approximation as we wish, - to an arbitrary reversible cycle superimposed on a family of isotherms.



We can approximate the actual cycle by connecting the isotherms by suitably chosen adiabatic lines, thus forming an assembly of Carnot cycles. The adjacent Carnot cycles have a common isotherm and the two travels; in opposite directions cancel each other in the region of overlap as far as heat transfer and work done are concerned. We can write then, for the isothermal-adiabatic sequence of lines as:

$$\sum \frac{Q}{T} = 0,$$

or in the limit of infinitesimal temperature differences between the isotherms:

$$\oint \frac{dQ}{T} = 0.$$

 ϕ indicates that the integral is evaluated for a complete traversal of the cycle, starting and ending at any arbitrary point of the cycle. If the integral of a quantity around any closed path is zero, the quantity is called state variable, that is, it has a value that is characteristic only of

the state of the system, regardless of how the state was arrived at. We call the variable in this case the entropy S.

$$dS = \frac{\delta Q}{T}$$
, and $\oint dS = 0$.

As we have already seen in conservative fields:

$$\oint dS = \int_{\substack{A \\ (g_1)}}^{B} dS + \int_{\substack{B \\ (g_2)}}^{A} dS = 0$$

$$\int_{\substack{A \\ (g_1)}}^{B} dS - \int_{\substack{A \\ (g_2)}}^{B} dS = 0,$$

SO

$$\int_{A\atop (g_1)}^{B} dS = \int_{A\atop (g_2)}^{B} dS.$$

This equation tells us that the change of the entropy between any two equilibrium states is independent of the path connecting those states. The change in entropy between *A* and *B* where the integral is evaluated over any reversible path connecting there two states:

$$S_B - S_A = \int_A^B dS = \int_A^B \frac{\delta Q}{T}$$
 (reversible process)

3.12.1 The second law of thermodynamics

The first law of thermodynamics expresses the conservation of energy in thermodynamic processes, but the first law cannot answer the direction of thermodynamic processes.

There are several statements as the second law but all of them are equivalent.

The second law of thermodynamics states:

It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts it completely into mechanical work, while ending in the same state in which it began.

In other words: it is impossible in principle for any heat engine to have a thermal efficiency of 100%.

3.12.2 The Efficiency of Engines

We have already seen the efficiency of a reversible Carnot cycle. The result we have got:

$$e = 1 - \frac{T_C}{T_H} = 1 + \frac{Q_C}{Q_H}$$
.

Carnot stated the next theorem:

All Carnot engines operating between the same two temperatures have the same efficiency, irrespective of the nature of the working substance. The efficiency of all reversible engines performing a Carnot cycle between the same temperatures is the same, and no irreversible engine working between the same two temperatures can have a greater efficiency than this:

$$e_{irr} \leq e_{rev}$$
.

Consider an irreversible Carnot cycle (suppose that the piston moves with friction during the process). In this care the absorbing heat Q_H decreases and Q_C the rejected heat increases:

$$e = 1 + \frac{Q_C'}{Q_H'} \le 1 - \frac{T_C}{T_H},$$

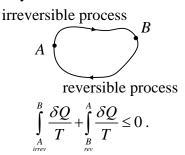
that is

$$\frac{Q_C'}{T_C} + \frac{Q_H'}{T_H} \le 0,$$

so for the cyclic process:

$$\oint \frac{\delta Q}{T} \le 0$$

Consider now the next irreversible cycle:



We can change the direction of a process in case of a reversible process.

$$\int_{A}^{B} \frac{\delta Q}{T} - \int_{A}^{B} \frac{\delta Q}{T} \leq 0,$$

$$\int_{A}^{B} \frac{\delta Q}{T} \leq \int_{A}^{B} \frac{\delta Q}{T}.$$

but for a reversible process this is just the change of entropy, so

$$\int_{A}^{B} \frac{\delta Q}{T} \leq S_{B} - S_{A} .$$

The change of the entropy in case of an irreversible process is always greater than the integral of $\frac{\delta Q}{T}$. If the process is reversible then the change of the entropy equals to the integral.

3.12.3 Entropy and the second low

If we consider a system which is adiabatically isolated form the surrounding that is:

$$\delta Q = 0$$
,

then

$$S_B - S_A \underset{rev.process}{\geq} 0$$
,

or

$$S_B - S_A = 0$$
, reversible adiabatic process and $S_B - S_A > 0$, irreversible adiabatic process

Thus, when an irreversible process occurs in an isolated system, the entropy grows. The entropy of a system in its equilibrium state is maximum. This statement is just one form of the Second Law of thermodynamics.