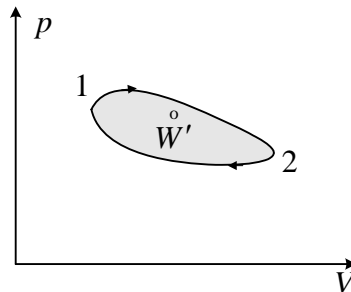


4.7 Cyclic process

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

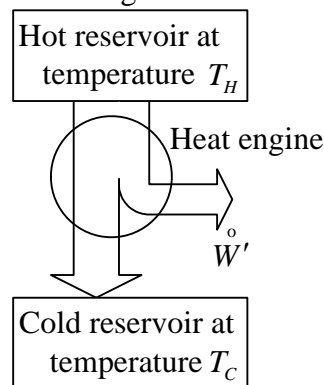


When a system is carried through a cyclic process its initial and final internal energies are equal. So the total internal-energy change in any cyclic process is zero. Apply the first law for a cyclic process:

$$\begin{aligned}\Delta E &= \overset{\circ}{Q} + \overset{\circ}{W} \\ \Delta E &= 0, \\ \overset{\circ}{W}' &= \overset{\circ}{Q}.\end{aligned}$$

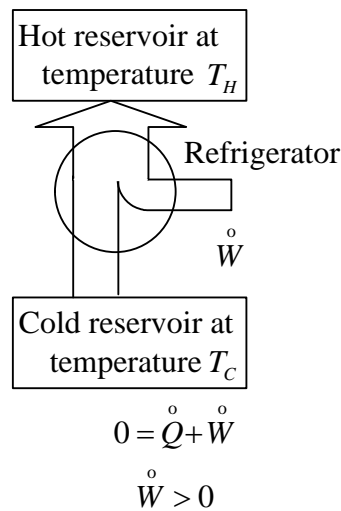
The work done by the system in a cyclic transformation is equal to the heat absorbed by the system.

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:



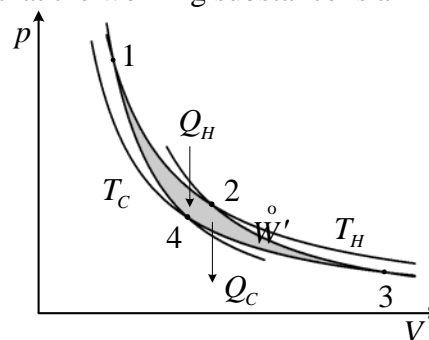
$$\begin{aligned}\overset{\circ}{W}' &> 0, \\ \overset{\circ}{Q} &= 0.\end{aligned}$$

Refrigerator is a heat engine operating in reverse. It takes heat from a hot place and gives off heat to a colder 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 than taken from the cold reservoir.



4.7.1 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_C , rejecting heat Q_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:

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

where Q_H is the absorbing heat, and \dot{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:

$$T_H V_1^{\kappa-1} = T_C V_4^{\kappa-1}$$

$$T_H V_2^{\kappa-1} = T_C V_3^{\kappa-1},$$

$$\frac{V_1}{V_2} = \frac{V_4}{V_3},$$

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.

4.8 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:

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

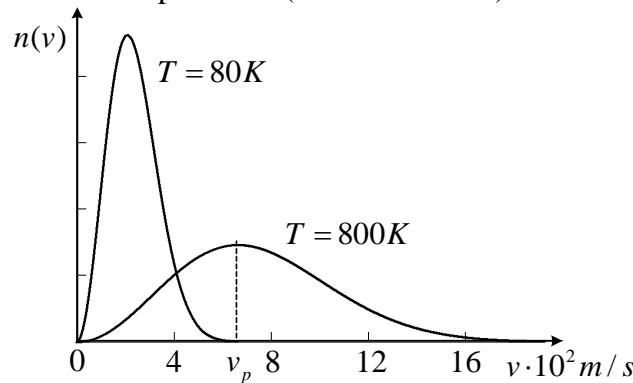
as

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

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:

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

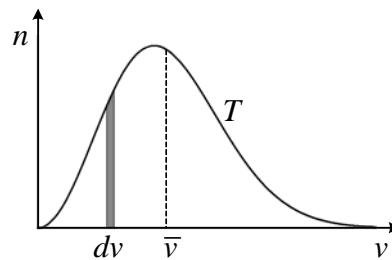
The distribution curve is not symmetrical about the most probable speed. Without proof:

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

The average speed is defined as:

$$\bar{v} = \frac{1}{N} \int_0^{\infty} n(v) v dv,$$

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:

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

Also the integral of the quantity $v^2 n(v)$ 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:

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

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

$$N = \int_0^{\infty} n(v) dv.$$

4.9 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.

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

The unit of α is:

$$[\alpha] = \frac{1}{K} = \frac{1}{^\circ C}$$

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:

$$\begin{aligned}A &= A_0 + \Delta A = a(1 + \alpha \Delta T)b(1 + \alpha \Delta T), \\ A_0 + \Delta A &= ab(1 + 2\alpha \Delta T + \alpha^2 \Delta T^2), \\ A_0 + \Delta A &= A_0 + A_0(2\alpha \Delta T + \alpha^2 \Delta T^2), \\ \Delta A &= A_0(2\alpha \Delta T + \alpha^2 \Delta T^2).\end{aligned}$$

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 isotropic 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.

$$\begin{aligned}\Delta V &= \beta V_0 \Delta T, \\ V &= V_0 + \Delta V = V_0 (1 + \beta \Delta T)\end{aligned}$$

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:

$$V_0 = a \cdot b \cdot c$$

$$V_0 + \Delta V = a(1 + \alpha\Delta T)b(1 + \alpha\Delta T)c(1 + \alpha\Delta T),$$

$$V_0 + \Delta V = abc(1 + 3\alpha\Delta T + 3\alpha^2\Delta T^2 + \alpha^3\Delta T^3),$$

$$\Delta V = V_0(3\alpha\Delta T + 3\alpha^2\Delta T^2 + \alpha^3\Delta T^3).$$

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 $3\alpha^2\Delta T^2 \ll 3\alpha\Delta T$.

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

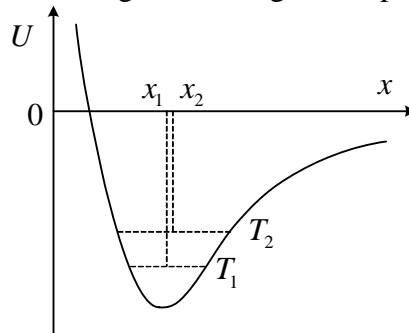
we obtain:

$$\beta = 3\alpha.$$

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.

4.9.1 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.

4.10 Heat transfer

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

4.10.1 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:

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

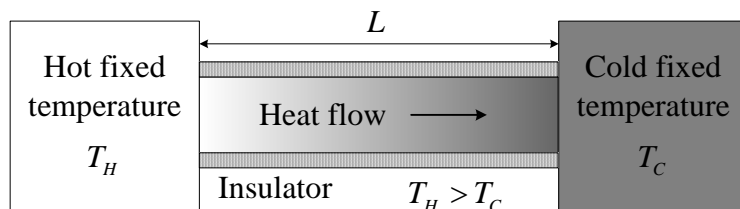
H is the time rate of heat transfer across the area A . The quantity $\frac{dT}{dx}$ is called temperature gradient. k is the thermal conductivity, its numerical value depends on the material of the slab. Taking a unit cross-sectional area:

$$h = -k \nabla T$$

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:

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

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:

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

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

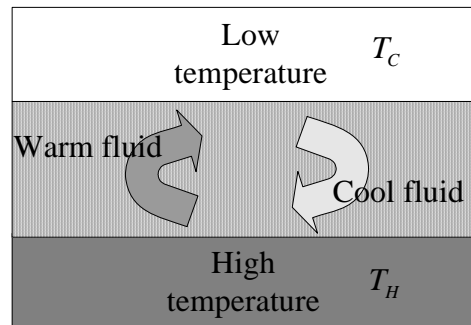
Finally the heat current density:

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

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

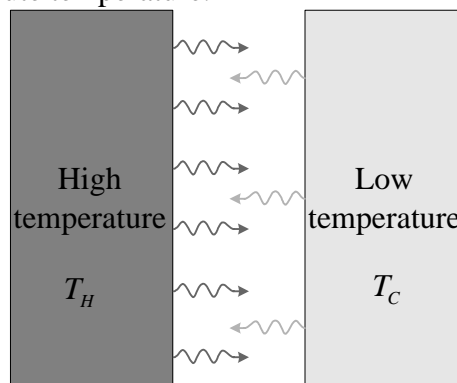
4.10.2 Convection

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.



4.10.3 Radiation

Radiation is when the heat is transferred by electromagnetic radiation. All objects 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.

4.11 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 points 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:

- it can be carried out with equal ease in two opposite directions,
- in each case the system passes through the same intermediate states,
- after carrying out the direct and reverse processes, the system and the surroundings 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.

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

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

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

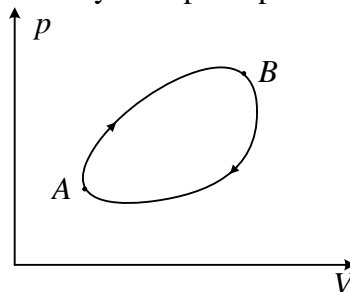
It means that:

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

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

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:

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

\oint 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 .

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

As we have already seen in conservative fields:

$$\begin{aligned} \oint dS &= \int_{A(g_1)}^B dS + \int_{B(g_2)}^A dS = 0 \\ \int_{A(g_1)}^B dS - \int_{A(g_2)}^B dS &= 0, \end{aligned}$$

so

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

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 these two states:

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

4.11.1 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 %.

4.11.2 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 case the absorbing heat Q_H decreases and Q_C the rejected heat increases:

$$e = 1 + \frac{Q'_C}{Q'_H} \leq 1 - \frac{T_C}{T_H},$$

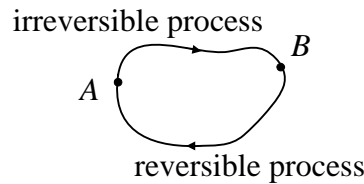
that is

$$\frac{Q'_C}{T_C} + \frac{Q'_H}{T_H} \leq 0,$$

so for the cyclic process:

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

Consider now the next irreversible cycle:



$$\int_{A \text{ irrev}}^B \frac{\delta Q}{T} + \int_{B \text{ rev}}^A \frac{\delta Q}{T} \leq 0.$$

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

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

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

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

$$\int_{A \text{ irrev}}^B \frac{\delta Q}{T} \leq S_B - S_A.$$

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.

4.11.3 Entropy and the second law

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

$$\delta Q = 0,$$

then

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

or

$$S_B - S_A = 0, \text{ reversible adiabatic process}$$

$$\text{and } S_B - S_A > 0, \text{ irreversible adiabatic process}$$

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.