A Carnot engine can only be approximated by engineering and in practice it is not a useful device to deliver work. However, the Carnot efficiency is very important, because it gives us an upper limit on the efficiencies of all heat engines.

The Absolute Temperature Scale:

Since the Carnot efficiency depends only on the ratio of the temperatures of two heat reservoirs, the Carnot machine can be used to define the ratio of temperatures independently of the properties of any substance:

$$\frac{T_{\mathrm{c}}}{T_{\mathrm{h}}} = \frac{|Q_{\mathrm{out}}|}{Q_{\mathrm{in}}}$$

where $|Q_{\mathrm{out}}|$ and Q_{in} are the thermal energies transferred by a Carnot machine. The absolute temperature is then completely determined by the choice of one reference point.

Heat Pumps

A heat pump is essentially a refrigerator that is used to pump thermal energy from a cold reservoir to a hot reservoir. Using $W = |Q_\mathrm{h}| - Q_\mathrm{c}$, we can calculate the maximum coefficient of performance:

$$\mathrm{COP} = \frac{Q_\mathrm{c}}{W} = \frac{Q_\mathrm{c}}{|Q_\mathrm{h}| - Q_\mathrm{c}} = \frac{Q_\mathrm{c}/|Q_\mathrm{h}|}{1 - Q_\mathrm{c}/|Q_\mathrm{h}|}$$

and for the Carnot cycle

$$\mathrm{COP}_\mathrm{max} = \frac{T_\mathrm{c}/T_\mathrm{h}}{1 - T_\mathrm{c}/T_\mathrm{h}} = \frac{T_\mathrm{c}}{T_\mathrm{h} - T_\mathrm{c}} = \frac{T_\mathrm{c}}{\triangle T}\ .$$

For a heat pump one is interested in the amount of work needed to put a certain amount of heat Q_h into the hot reservoir (the room to be heated). We find this from

$$\mathrm{COP} = \frac{Q_\mathrm{c}}{W} = \frac{|Q_\mathrm{h}| - W}{W}$$

$$W\,(\mathrm{COP} + 1) = |Q_\mathrm{h}| \ \Rightarrow\ W = \frac{|Q_\mathrm{h}|}{1 + \mathrm{COP}}\ .$$

Irreversibility and Disorder

Figures 20-9 illustrate how a system moves to a less ordered state in an irreversible process.

A box containing a gas of mass M at temperature T moves along a frictionless table and has an inelastic collisions with a wall.

Before the collision the center-of-mass (cm) energy $M\,v_{\rm cm}^2/2$ is ordered mechanical energy that could be converted to work, while the energy of the molecule motions with respect to the cm is internal energy related to the temperature of the gas.

The inelastic collision converts the ordered mechanical energy into random internal energy and the temperature of the gas rises.

Entropy

Entropy S is a measure of the disorder of the system. Like the pressure P, the volume V, the temperature T and the internal energy U, the entropy is a function of the state of the system (thermodynamic function). As with potential energy, it is the change in the entropy that is important. It is defined by

$$dS = \frac{dQ_{\text{rev}}}{T}$$

where dQ_{rev} is the heat that must be added to the system in a reversible process to bring the system from the initial state to the final state (dQ_{rev} can be negative). The equation is a method for calculating the entropy. It does not mean that a reversible process has actually to be used in Lab experiments or by nature.

Entropy of an Ideal Gas

We consider a reversible quasi-static process in which the system absorbs an amount of heat

$$dQ = dU + dW = C_V\, dT + n\, R\, T\, \frac{dV}{V}\ .$$

This equation can only be integrated, if we know how T depends one V. But if we divide each term by T, we obtain

$$dS = \frac{dQ}{T} = C_V \frac{dT}{T} + n\,R \frac{dV}{V}$$

and this equation can be integrated since C_V depends only on T. For simplicity we assume that C_V is a constant and find

$$\triangle S = \int_1^2 \frac{dQ}{T} = C_V \ln\left(\frac{T_2}{T_1}\right) + n\,R \ln\left(\frac{V_2}{V_1}\right) \ .$$

Isothermal Expansion of an Ideal Gas:

The entropy change is

$$\triangle S = n\,R \ln\left(\frac{V_2}{V_1}\right) > 0 \ .$$

In this process an amount of heat leaves the reservoir and enters the gas. It equals the work done by the gas:

$$Q = W = \int_1^2 P\,dV = n\,R\,T \int_1^2 \frac{dV}{V} = n\,R\,T \ln\left(\frac{V_2}{V_1}\right) \ .$$

The entropy change of the gas is Q/T and the entropy change of the reservoir is $-Q/T$. Therefore, the net entropy change of the gas plus the reservoir is zero. This illustrates a general result:

In a reversible process, the entropy change of the system and its surroundings (universe) is zero.

Free Expansion of an Ideal Gas:

This is an irreversible process. Since the change in the entropy of a system depends only on the initial and final states, the entropy change of the gas for the free expansion is the same as for the isothermal expansion:

$$\triangle S_{\rm gas} = n\,R\,\ln\left(\frac{V_2}{V_1}\right)\ .$$

In this case there is no change of the surrounding, so the entropy of the system and its surroundings increases by $\triangle S = \triangle S_{\rm gas} > 0$. The general result is:

In an irreversible process, the entropy of the system and its surroundings increases.

Yet another formulations of the second law of thermodynamics is then:

For any process the entropy of the system and its surroundings never decreases.

Constant Pressure Processes:

$$dQ = C_P\, dT \;\; \Rightarrow$$

$$\triangle S = C_P \int_{T_1}^{T_2} \frac{dT}{T} = C_P \ln\left(\frac{T_2}{T_1}\right) \; .$$

As this process is accompanied by the work $P\triangle V$, the entropy of the surroundings changes too.

Inelastic Collision:

Example: Fall of a body from height h:

$$\triangle S = \frac{Q}{T} = \frac{m\,g\,h}{T} \; .$$

There is no entropy change of the surroundings in this case.

Heat Conduction from One Reservoir to Another:

As heat conduction is an irreversible process, we expect the entropy of the system (hot and cold reservoir) to increase. The hot reservoir looses heat Q, so its entropy change is

$$\triangle S_h = -\frac{|Q|}{T_h} \; .$$

The cold reservoir absorbs the heat Q, so its entropy change is

$$\triangle S_c = -\frac{|Q|}{T_c} \ .$$

The net entropy change of the combined system is

$$\triangle S = \triangle S_c + \triangle S_h = \frac{|Q|}{T_c} - \frac{|Q|}{T_h} > 0$$

where the inequality is implied by $T_h > T_c$.

Carnot Cycle:

As a Carnot cycle is by definition reversible, the entropy change of the Carnot machine and its surroundings must be zero after one cycle. The explicit calculation is:

$$\triangle S = -\frac{|Q_{\rm h}|}{T_h} + \frac{|Q_{\rm c}|}{T_c} = 0$$

because $|Q_{\rm h}|/|Q_{\rm c}| = T_h/T_c \Rightarrow |Q_{\rm h}|/T_h = |Q_{\rm c}|/T_c$.

Entropy and the Availability of Energy

In our example of an inelastic collisions the loss of energy available for work was

$$W_{\text{lost}} = m\,g\,h = T\,\triangle S\ .$$

This is a general result:

In an irreversible process, energy equal to $T\,\triangle S$ becomes unavailable for doing work, where T is the temperature of the coldest reservoir of the system.

Examples:

In the free expansion of an ideal gas the change of entropy was $n\,R\,\ln(V_2/V_1)$, so the work lost is $n\,R\,T\,\ln(V_2/V_1)$. This is precisely the work that the gas could have done at constant temperature:

$$W = \int_1^2 P\,dV = n\,R\,T \int_1^2 \frac{dV}{V} = n\,R\,T\,\ln\left(\frac{V_2}{V_1}\right)\ .$$

When heat is conducted from a hot to a cold reservoir, the work lost is

$$W_{\mathrm{lost}} = T_c \triangle S = T_c \left(\frac{|Q|}{T_c} - \frac{|Q|}{T_h} \right) = |Q| \left(1 - \frac{T_c}{T_h} \right) \ .$$

This is precisely the work that could have been done by running a Carnot engine between the two reservoirs.

Entropy and Probability

Let us consider the free expansion of a gas from an initial volume V_1 to a final volume $V_2 > V_1$. The entropy change of this systems is

$$\triangle S = n\,R\,\ln\left(\frac{V_2}{V_1}\right) \ .$$

Why is this process irreversible? Why can't the gas compress by itself back to the volume V_1? The reason is that this is merely very improbable. Assume the gas consists of N molecules. The probability p of finding all N molecules in the smaller volume is

$$p = \left(\frac{V_1}{V_2}\right)^N \ .$$

Taking the logarithm on both sides, we obtain

$$\ln(p) = N\,\ln\left(\frac{V_1}{V_2}\right) = -n\,N_A\,\ln\left(\frac{V_2}{V_1}\right)$$

where n is the number of moles and N_A is Avogadro's number.

Hence, we can write the change in entropy as

$$\triangle S = -\frac{R}{N_A}\,\ln(p) = -k\,\ln(p)$$

where k is Boltzmann's constant. The change in entropy is the Boltzmann constant time the negative logarithm of the probability that the gas assembles spontaneously in the smaller volume.

Note that some cosmological scenarios predict a contraction of the universe after a period of expansion. So, one has to be very cautious when applying the entropy concept beyond its established range of validity, namely closed thermodynamical systems, which can reach equilibrium. The universe as a whole may or may not move towards a final equilibrium state (simply nobody knows).