Lecture 2.7
Entropy and the Second law of Thermodynamics

During last several lectures we have been talking about different thermodynamic processes. In particular, we have discussed heat transfer between the different objects. We have learned about the first law of thermodynamics, which is essentially the law of conservation of energy for any thermodynamic processes. No one process can exist in nature which does not obey this law. However, there are processes, obeying the first law of thermodynamics, and yet they do not exist. For instance: (1) A crate sliding over an ordinary surface eventually stops and temperature of the surface increases. During this process the mechanical energy of the crate is transferred into internal energy of the crate-surface system. There is nothing wrong from the energy stand point for this crate, initially being at rest, to start sliding over the surface decreasing its temperature. However, we know that this never happens. (2) If you drop a metal sphere to the floor, it will stay there as a result of inelastic collision. The temperature of the system will increase. But this sphere will never jump up from the floor decreasing its temperature. (3) Some gas which has expanded into the empty space is not coming back to the smaller container by itself. (4) The glass broken into small pieces is not coming back together. All these examples show that some processes in nature can only occur in certain direction, but they cannot take place in the opposite direction. These are examples of irreversible processes. Neither the law of conservation of energy, nor Newtonian mechanics prohibits the existence of reverse processes, but there is something else which does.

All the systems, which we just considered, are the closed systems. As we saw before, in these systems the internal energy of different parts of the system can change in any direction, it can either grow or decrease as long as the total energy of the system is conserved. Therefore, there is another function of state, known as entropy, which is responsible for direction of any thermodynamic process. The entropy of the closed system always increases in irreversible process, it never decreases. In reversible processes in the closed systems, the entropy does not change at all, but no one process where it decreases can exist.
Let us see, how we can define the entropy. The perfect example of irreversible process is the free expansion of ideal gas. In this example we have a gas, which was originally placed in some volume \( V_1 \) and it was allowed to expand quickly to the larger volume \( V_2 \). We have already discussed that this is an example of nonequilibrium process. So, we can only talk about the values of thermodynamic variables in the original and the final states of this gas, but not during the process itself. We described the state of this gas by means of two variables: volume and pressure. Now, we will introduce one more variable, known as entropy. The differential change of entropy \( dS \) in reversible process is defined as

\[
dS = \frac{\delta Q}{T},
\]

so the change of entropy during some reversible process is

\[
\Delta S = S_2 - S_1 = \int_{1}^{2} dS = \int_{1}^{2} \frac{\delta Q}{T}.
\]

Here \( \delta Q \) is the elementary heat supplied to the system or taken from the system during the process. However, in the case of the free expansion we cannot use this definition of entropy to calculate its change. This is because during the non-equilibrium process we cannot establish the relationship between \( \delta Q \) and \( T \). On the other hand, we have said that entropy is the state function, so its change should not depend on the process. It only depends on the original and the final states of the system. So, instead of the free expansion, let us use some other reversible process, but in such a way that it connects the same original and final states on the \((p, V)\) diagram, so it has the same change of entropy. We have already proven that the temperature of ideal gas is not changing during its free expansion, so one can connect the original and the final state on the \((p, V)\) diagram by the reversible isotherm. Moreover, since the temperature is constant, we can take it outside of integration sign, which gives

\[
\Delta S = \frac{1}{T} \int_{1}^{2} dQ = \frac{Q}{T},
\]

where \( Q \) is the total heat transferred to this gas in such isothermal process. To keep the gas temperature constant, we have to supply heat to this gas, so \( Q > 0 \). This means that
entropy of the gas is increasing in the isothermal process as well as during its free expansion.

We have already mentioned that entropy, as well as other thermodynamic variables, such as volume, pressure and internal energy is function of state. Even though we will not prove this in general, let us make sure that it is true at least for ideal gas. We shall consider some slow (equilibrium) process for ideal gas. For every small part of this process we can apply the first law of thermodynamics in its differential form, which gives

\[ dE = \delta Q - \delta W \]

In the case of the equilibrium process for ideal gas this becomes

\[ \delta Q = dE + \delta W = nC_v dT + pdV, \]

so for differential of entropy we have

\[ dS = \frac{\delta Q}{T} = \frac{nC_v dT}{T} + \frac{pdV}{T} = nC_v \frac{dT}{T} + nR \frac{dV}{V}. \]

The entropy change of ideal gas then will be

\[ \Delta S = \int_{T_1}^{T_2} \left( nC_v \frac{dT}{T} + nR \frac{dV}{V} \right) = nR \ln \left( \frac{V_2}{V_1} \right) + nC_v \ln \left( \frac{T_2}{T_1} \right). \]  \tag{2.7.3}

This entropy change does not depend on the path of integration. It only depends on the original and final values of the gas’ volume and temperature. So, the entropy is the function of ideal gas’ state.

In this example the entropy of ideal gas has increased during the process of isothermal expansion. You might ask, what will happen if we compress this gas to its original state using the same isothermal procedure? We just proved that entropy is function of state. If we bring this gas back to its original state, then according to equation 2.7.3, entropy of the gas will decrease. So, how about the postulate that entropy can not decrease? There is no problem with it, because this postulate works only for closed systems. If we perform this compression, the gas in the container is not a closed system, since we have to apply an external force in order to compress the gas, and the heat released by the gas is absorbed by the container. In this case the gas’ entropy can decrease but not the total entropy of the gas-container system. The change of the gas
entropy during this isothermal process is $\Delta S_{gas} = -\frac{|Q|}{T}$, where $|Q|$ is the absolute value of the heat released by the gas. At the same time the entropy of the reservoir will increase by

$\Delta S_{res} = \frac{|Q|}{T}$, since this reservoir absorbs the heat from the gas. This means that the net entropy of the system is not changing. So, *if the process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.* This statement is also known as one of the forms for the *second law of thermodynamics*, which is

$$\Delta S \geq 0.$$ (2.7.4)

In reality all the processes in closed systems are somewhat irreversible, because they involve friction, turbulence and other factors. So, for any real process in the closed system the entropy always grows.

Let us now see why the subject of entropy is so important for the real life. We shall learn this on the example of a device known as an *engine*. If you ever looked inside of your car then you know what the engine is. It is a device which extracts energy from environment (fuel) in the form of heat and performs useful work out of that. Inside of every engine there is a working substance (air-gasoline mixture in the case of the car’s engine). To perform work on the regular basis, the working substance of the engine should return to its original state. So, the engine works through a cycle. In such a cycle the working substance passes through a series of thermodynamic processes, known as strokes.

Let us consider an *ideal engine*, which is also known as the *Carnot engine*. In this engine all the processes are reversible and no wasteful energy transfers occur due to friction or turbulence. During each cycle the working substance of the Carnot engine absorbs heat $|Q_H|$ from the thermal reservoir at constant high temperature $T_H$ and discharges heat $|Q_L|$ to a second heat reservoir at constant low temperature $T_L$. Heat $|Q_H|$ is transferred to the engine during isothermal expansion of the working substance from some original volume $V_a$ to another larger volume $V_b$. Then this working substance undergoes adiabatic expansion (no heat added during this process) to some even larger
volume \( V_c \). To bring the engine back to its original state, the heat \(|Q_L|\) transferred from the working substance to the heat reservoir during isothermal compression from \( V_c \) to a smaller volume \( V_d \). And finally the working substance is compressed back to its original volume \( V_a \) in adiabatic process without any additional heat released. During first two processes \( ab \) and \( bc \), the working substance is expanding, so it performs positive work. During the second two processes \( cd \) ad \( da \) the working substance is compressed, so it performs negative work. The net useful work performed by this engine is the difference between the work done by the substance in parts \( ab \) and \( bc \) and work done on the substance in parts \( cd \) and \( da \). This net work is positive and equal to the area enclosed by the cycle \( abcd \) on \((p, V)\) coordinate plane.

To calculate this work one can apply the first law of thermodynamics. Since this engine works through a closed cycle, the internal energy of the engine's working substance has not changed when it comes back to the same original state. In this case the first law of thermodynamics gives \( 0 = \Delta E = Q - W \), which means that the net work performed by the engine is equal to the net heat adsorbed by a working substance, which is

\[
W = Q = |Q_H| - |Q_L|.
\]

We also saw that changes of entropy for the system are closely related to the heat transferred to and from the system. Let us see what the change of entropy for the Carnot cycle is. During the two parts of this cycle we had adiabatic processes. In such a process the heat was neither supplied nor lost by the working substance, so its entropy has not changed. In other two isothermal parts of this cycle the change of entropy can be easily calculated, which is

\[
\Delta S = \Delta S_H + \Delta S_L = \frac{|Q_H|}{T_H} + \frac{|Q_L|}{T_L}.
\]

On the other hand the entropy is the state function, so it should not change at the end of complete reversible cycle such as Carnot cycle, this means that

\[
\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}.
\]
The purpose of any engine is to transform as much energy from the supplied heat $Q_H$ to the useful work as possible. This success is measured by the thermal efficiency $\varepsilon$, which is

$$
\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|}.
$$

(2.7.5)

In the case of the Carnot engine, that becomes

$$
\varepsilon_C = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H}.
$$

(2.7.6)

Since we always have $T_L < T_H$, the Carnot engine has efficiency less than 1, but larger than zero. So, only some part of energy extracted from the heater can be converted into useful work, another part of this energy is delivered to the low-temperature reservoir as heat $|Q_L|$. The perfect engine should have $Q_L = 0$, so it could be 100% efficient and would convert all the given energy into the useful work. However, this is impossible. There is no perfect engine. *No series of processes is possible whose sole result is the transfer of energy as heat from a thermal reservoir and the complete conversion of this energy to work.* This statement is another way to formulate the second law of thermodynamics. We shall prove this in a few moments. The ideal Carnot engine, which we just discussed, is the most efficient engine, which one can ever build. All other engines are even less efficient. If cars were powered by Carnot engines, they would be about 55% efficient. However, the real cars are about 25% efficient.

Another application of this theory is a refrigerator, which is a device that uses work to transfer energy from the low-temperature reservoir to the high-temperature reservoir. We shall consider the ideal refrigerator, in which all the processes are reversible and no wasteful energy transfers due to friction or turbulence occur. This ideal refrigerator can operate over reversed Carnot cycle, so it will be the Carnot refrigerator. In this case we would like to extract as much heat $|Q_L|$ as possible from the low-temperature reservoir for the least amount of work, coefficient of performance (efficiency) for refrigerator is

$$
K = \frac{|Q_L|}{|W|}.
$$

(2.7.7)
In the case of the ideal Carnot refrigerator, it becomes
\[ K_C = \frac{|Q_L|}{|Q_H|-|Q_L|} = \frac{T_L}{T_H-T_L}. \] (2.7.8)

In the case of the perfect refrigerator, it will not require any work, so \( |Q_L| = |Q_H| = |Q| \).
This, however, is also impossible. Indeed, we have already seen that the entropy of the working substance has not changed through the Carnot cycle, but the entropies of the reservoirs have changed. The net entropy change for the case of the perfect refrigerator is
\[ \Delta S = \frac{|Q|}{T_L} + \frac{|Q|}{T_H}. \]

As far as \( T_H > T_L \), the entropy will decrease, which contradicts the second law of thermodynamics, which can now be formulated as *no series of processes is possible whose sole result is the transfer of energy as heat from a reservoir at given temperature to a reservoir at higher temperature*.

Let us prove that Carnot engine is the most efficient one. Suppose that there is another engine with efficiency \( \varepsilon > \varepsilon_C \). We can couple this other engine with Carnot refrigerator, so the work performed by this new engine goes completely to the Carnot refrigerator and
\[ \varepsilon > \varepsilon_C, \]
\[ \frac{|W|}{|Q_H'|} > \frac{|W|}{|Q_H|}, \]
\[ |Q_H| > |Q_H'|, \]
where \( |Q_H'| \) is received from the heater by this new engine. On the other hand
\[ W = W, \]
\[ |Q_H| - |Q_L| = |Q_H'| - |Q_L'|, \]
\[ |Q_H| - |Q_H'| = |Q_L| - |Q_L'| = Q \]
The last quantity \( Q \) must be positive, and this heat is transferred from the low temperature reservoir to the high-temperature reservoir, which is impossible according to the second law of thermodynamics. So no engine can have efficiency higher than that of the Carnot engine.