CHAPTER V

Second Law of Thermodynamics

The first law of thermodynamics is a representation of the conservation of energy. It is a necessary, but not a sufficient, condition for a process to occur. Indeed, no restriction is imposed by the first law on the direction of the process: this is the role of the second law.

To illustrate this, let us assume the processes below, in your opinion, without any intervention from you, what is the most probable process (from left to right or the inverse):

1. HOT to COLD
2. ?
3. ?
4. HOT to COLD

Second Law of Thermodynamics
Consider now the following arrangement:

Allowing the weight to fall will turn the paddlewheel which will do work on the fluid system. Initially this may increase the kinetic energy of the fluid as it churns, but in time the circulation will stop. When this happens the temperature of the fluid will rise and the heat will be transferred to the surroundings.

From a 1\textsuperscript{st} Law perspective there is no reason why one could not simply supply this same amount of heat to the fluid so that the paddlewheel would turn and the weight would be raised. However, no one has ever built a successful engine based on this principle. It simply wouldn’t work. The 2\textsuperscript{nd} Law provides us with a basis to determine why such a process isn’t feasible.

I. Heat Engines

While the 2\textsuperscript{nd} Law of Thermodynamics is applicable to a wide range to topics, much of our understanding of the principle comes from the study of heat engines. We will therefore use engines as a basis for much of our study.
In this cycle air will circulate through the heat engine to transport energy from one component to the next. This fluid is often referred to as the working fluid.

\[ W_C = \text{Work required to compress the working fluid} \]
\[ W_T = \text{Usable work produced by the engine. This work may be used to drive a truck or car, turn a propeller, an electric generator or to perform some other useful task.} \]

\[ Q_{\text{in}} = \text{Thermal energy supplied to the system. This may arise from combustion, a solar collector, a nuclear reactor or any other available heat source.} \]
\[ Q_{\text{out}} = \text{Thermal energy rejected to the environment. The cooler could be a radiator similar to that used with an automobile engine.} \]

Since operation of the engine requires a work input to turn the compressor, a portion of the output work may be utilized for this purpose, we define, therefore, the net work as:

\[ |W_{\text{net}}| = |W_T| - |W_C| \]

This is a thermodynamic cycle. By definition the cycle begins and ends at the same point. In the case of an open cycle heat rejection occurs as the exhaust is emitted into the atmosphere. Hot exhaust gases are cooled to the temperature of the surroundings before entering the compressor.

From the 1\textsuperscript{st} Law of Thermodynamics, we have:

\[ \Delta E_{\text{system}} = Q_{\text{in}} - W_{\text{out}} \]

For the cycle, since the starting and ending points are the same, there is no change in internal energy, so:

\[ W_T - W_C = Q_{\text{in}} - Q_{\text{out}} \]

I.1. Cycle Diagram

It is very convenient to represent the heat engine processes on a PV diagram:
I.2. Thermal Efficiency of a heat engine

The efficiency of a heat engine can be defined as the ratio of the useful work out (the net work) to the energy that must be input (the energy that we pay for).

\[ \eta = \frac{W_{\text{net}}}{Q_{\text{in}}} \]

Since we have that \( W_{\text{net}} = Q_{\text{in}} - Q_{\text{out}} \), we may substitute into the above equation and find:

\[ \eta = \frac{(Q_{\text{in}} - Q_{\text{out}})}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} \]

It is probably not too surprising that we want to minimize the fraction of rejected heat in the last part of the equation in order to attain the maximum efficiency.

I.3. Second law of Thermodynamics: Kelvin-Planck statement

In the drawing above, a piston-cylinder contains a gas at 30°C. A weight is placed on the piston. Heat is then added to the gas from a reservoir at 100°C so that the gas expands. As the gas expands it does work to raise the weight and piston.

The weight now is at a higher potential energy than at state one. We slide the weight off of the piston at the higher elevation. Assume that the frictional forces in sliding the weight are negligible.

Now, we wish to raise a second weight. That is, we wish the heat engine to continue to do work. The gas inside the cylinder is still heated and will not return to its initial position unless the gas is cooled.

If you consider the gas turbine cycle and the piston-cylinder arrangement, in both cases we have seen that it is necessary to reject heat at the end of the work process in order to return the cycle to its initial state and repeat the process. We generalize this observation as the 2nd Law of Thermodynamics:

Second Law of Thermodynamics
I.4. Refrigeration Cycles and Clausius statement of the second law of Thermodynamics

Up to this point we have only considered heat engines. Refrigeration cycles operate in a similar manner.

The vapor refrigeration cycle involves four components, designed to produce four respective processes on the working fluid.

- (Process 1-2) The compressor is designed to raise the pressure of the working fluid adiabatically. As the vapor is compressed, the temperature will rise.
- (Process 2-3) The fluid is passed through the condenser. Here no work is done on the fluid, but it is cooled to a saturated liquid. (This is the part of a residential AC unit which is located outdoors. Air is circulated around tubes containing the working fluid by a fan.)
- (Process 3-4) An expansion valve is simply a device, which does no work, nor does it transfer heat to or from the working fluid. It is simply a device to allow the pressure to drop to a lower value. A First Law analysis of this process will show that it is a constant enthalpy process. It is common for some of the liquid to flash to vapor as the fluid expands. At the same time, the temperature will drop significantly.
- (Process 4-1) The fluid is passed through the evaporator. This device consists of cold tubes often seen located inside the house in a residential unit. Here air from inside the house is blown over the cold tubes containing the working fluid. As the cold fluid gains heat, no work is done on the fluid. The working fluid is largely vaporized in this process as it returns to state 1 to begin the cycle again.

You can imagine that in a refrigeration cycle, heat will not flow from a low temperature to a high temperature without work. We see the input of work in the basic refrigeration cycle in operating
the compressor. This principle is accepted as an alternate statement of the Second Law of Thermodynamics.

\[ \text{\textit{It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.}} \] -- Clausius statement of 2nd Law.

The two statements of the 2nd Law can be shown to be equivalent.

**Practical statement of the second law of Thermodynamics**

In the normal course of events, when things are not actively maintained, they deteriorate. Suns burn out, mountains crumble, cars rust, houses fall down, etc. The reverse process does not happen without intervention. You might buy an old, rusty car and restore it, but it will take work. In a like fashion, process involving an energy transfer will only occur in such a way so as to decrease the quality of energy. We can, within a finite control volume, transfer energy to the system so as to increase the quality of energy within that system. However, the work that we input required that we decrease the quality of energy from an area outside the system. When we consider the universe as a whole, the quality of energy in the universe has still deteriorated.

**I.4.1. Coefficient of performance**

When describing heat engines, we introduced the concept of engine efficiency as the desired output divided by the energy input. Similarly, we define the coefficient of performance (COP) of a refrigerator:

\[
COP = \frac{\text{Desired Output}}{\text{Required Input}} = \frac{Q_{14}}{W_{\text{net}}} = \frac{Q_{14}}{Q_{23} - Q_{14}}
\]

The definition is basically the same as that of thermal efficiency. The primary reason for the change in terminology is that a COP: is often greater than 1. The term is used to avoid speaking of any efficiency greater than 100%.

**I.5. Reversibility**

Consider a system of pulleys and weights as shown:

![Diagram of a pulley system with weights and a weight increment \( W + \delta W \).]

Second Law of Thermodynamics
In order for the weight on the right to raise the weight on the left, it is essential that $W + \delta W > W$. How large must $\delta W$ be? Well, it must be large enough that it compensates for the effects of friction in the pulley, the friction associated with the flexing of the cable, etc. If we use very good bearings, then the required extra weight on the right may approach zero. Can it reach zero? No, this would result in static equilibrium and the weights will no move. It is essential that $\delta W$ be greater than zero; it may approach, but never reach zero, even with perfect bearings.

We see that, in order for the process of raising the left weight to occur, the loss in potential energy on the right must be greater than the gain in potential energy on the left. As an idealization only, we may assume that the weight $\delta W$ may be so small that it can be treated as zero. In such a case, the weight on the right and left are equal and the direction that the pulley moves would be completely reversible. Such processes never occur in nature, but may be approached in the limit.