Chapter 5
The Second Law of Thermodynamics

5.1 Statements of The Second Law

Consider a power cycle shown in Figure 5.1-1a that has the following characteristics. The power cycle absorbs 1000 kJ of heat from a high temperature heat source and performs 1200 kJ of work. Applying the first law to this system we obtain,

$$\Delta E_{\text{cycle}} = Q_{\text{cycle}} + W_{\text{cycle}} \Rightarrow 0 = 1000 + (-1200) = -200 \text{ kJ}$$

This is obviously impossible and a clear violation of the first law of thermodynamics as 200 kJ of energy have been created.

![Figure 5.1-1](image)

(a) Violation of the first law
(b) Obey the first law

**Figure 5.1-1** (a) A power cycle receiving 1000 kJ of heat and performing 1200 kJ of work, which is a violation of the law of conservation of energy.
(b) A power cycle receiving 1000 kJ of heat and performing 1000 kJ of work, which does not violate the law of conservation of energy.

Consider next the power cycle shown in Figure 5.1-1b where the system absorbs 1000 kJ of heat from a high temperature heat source and performs 10200 kJ of work. Applying the first law to this system we obtain,

$$\Delta E_{\text{cycle}} = Q_{\text{cycle}} + W_{\text{cycle}} \Rightarrow 0 = 1000 + (-1000) = 0$$

The first law of thermodynamics is satisfied, and all would seem to be well. However, it is a fact that no one has ever succeeded in creating a device that will produce 1000 kJ of work from 1000 kJ of heat. If this were possible one can create a machine, a car for example, that could absorb a quantity of heat $Q_{\text{cycle}}$ from the environment and convert this heat energy into work to run the car and no fuel would be needed! But in spite of all such attempts, and the patent literature is full of such attempts, no device has ever been created to work in this way. We now give the *Kelvin-Planck statement* of the second law:

**It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir.**
Consider a heat pump operating as a cycle that has the following characteristics. The heat pump absorbs 1000 kJ of heat \( Q_C \) from a low temperature reservoir and delivers 1200 kJ of heat \( Q_H \) to a high temperature reservoir. The heat pump is shown in Figure 5.1-2a. Applying the first law to his system we obtain,

\[
\Delta E_{\text{cycle}} = Q_C - Q_H \Rightarrow 0 = 1000 - 1200 = -200 \text{ kJ}
\]

This is obviously impossible and a clear violation of the first law of thermodynamics as 200 kJ of energy have been created. This heat pump is called a perpetual motion machine of the first kind since it violates the first law of thermodynamics.

Consider next the heat pump shown in Figure 5.1-1b where the system absorbs 1000 kJ of heat \( Q_C \) from a low temperature reservoir and delivers 1000 kJ of heat \( Q_H \) to a high temperature reservoir. The heat pump is shown in Figure 5.1-2b. Applying the first law to his system we obtain,

\[
\Delta E_{\text{cycle}} = Q_{\text{cycle}} - Q_H \Rightarrow 0 = 1000 - 1000 = 0
\]

The first law of thermodynamics is satisfied, and all would again seem to be well. However, it is a fact that no one has ever succeeded in creating a cyclic device that will deliver 1000 kJ of heat to a higher temperature reservoir from a lower temperature reservoir without anything else happening. If this were possible one can create a machine that could absorb a quantity of heat \( Q_C \) from the earth and deliver this heat to our home to keep it warm and no fuel oil would be needed! But in spite of all such attempts, and the patent literature is full of such attempts, no device has ever been created to work in this way. This device is called a perpetual motion machine of the second kind since it violates the second law of thermodynamics. We now give the Clausius statement of the second law:

**It is impossible for any system to operate in such a way that the sole results would be an energy transfer by heat from a cooler to a hotter body.**
5.2 Applications of the Second Law to Thermodynamic Cycles

![Thermodynamic cycles diagram]

Figure 5.2-1 Thermodynamic cycles.

In a power cycle, the system receives heat from a high temperature source, produces work, and rejects some of the heat to a low temperature reservoir. In a refrigeration cycle, the system receives work to move heat from a low temperature source to a high temperature reservoir. In a heat pump cycle, the system receives work to move heat from a low temperature reservoir to a high temperature source. In a refrigeration cycle, the heat removed from the low temperature source is the main focus, while in a heat pump, the heat supplied to the high temperature source is the goal.

The performance of a thermodynamic cycle can be defined in terms of the ratio of the energy or work of interest to the energy or work supplied to the system. With the power cycle, we are interested in the work $W_{\text{cycle}}$ for the amount of heat $Q_H$ supplied to the system, therefore the thermal efficiency $\eta$ of the power cycle is defined as

$$\eta = \frac{W_{\text{cycle}}}{Q_H} = \frac{Q_H - Q_C}{Q_C} = 1 - \frac{Q_C}{Q_H} \quad (5.2-1)$$

From the definition, the thermal efficiency is always less than 1 since $Q_C$ must be greater than zero. With the refrigeration cycle, we are interested in the $Q_C$ removed from the low temperature source for the amount of work $W_{\text{cycle}}$ supplied to the system. The coefficient of performance $\beta$ for the refrigeration cycle is defined as

$$\beta = \frac{Q_C}{W_{\text{cycle}}} = \frac{Q_C}{Q_H - Q_C} \quad (5.2-2)$$

The coefficient of performance $\beta$ for the refrigeration cycle can be greater than 1. With the heat pump cycle, we are interested in the $Q_H$ supplied to the high temperature source for the amount of work $W_{\text{cycle}}$ supplied to the system. The coefficient of performance $\beta$ for the heat pump cycle is defined as
\[ \gamma = \frac{Q_H}{W_{cycle}} = \frac{Q_H}{Q_H - Q_C} \]  

(5.2-3)

The *coefficient of performance* \( \gamma \) for the heat pump cycle can never be less than 1. Since \( W_{cycle} \) must be greater than zero, the coefficient of performances must be finite in value.

### 5.3 Spontaneous and Reversible Processes

A spontaneous process is one that occurs of its own accord. We are familiar with many kinds of spontaneous processes. For example,

1) Heat flows from a higher to a lower temperature object.
2) Nitrogen from an opening of a high-pressure cylinder will spontaneously flow into the atmosphere.
3) The water in a river flows from upstream (higher elevation) to downstream (lower elevation).
4) A drop of black ink in a glass of water will spontaneously diffuse throughout the water and produce a uniform grayish solution.

A spontaneous process proceeds spontaneously in one direction only; it never proceeds spontaneously in the reverse direction. It should be noted that the reverse process can be made to happen by the application of external forces or “agents”.

A reversible process can be reversed at any point along its path by the application of an infinitesimal driving force in the opposite direction. If any part of the process, no matter how small, is not reversible, then the entire process is not reversible. A reversible process proceeds as the result of the application of infinitesimal small driving forces (either temperature, or pressure, or gravitational potential, or any other driving force). The application of an infinitesimal small driving force in the opposite direction will reverse the direction of the process. For a reversible process, both the system and surroundings can be returned to their initial states. A reversible process proceeds from start to finish by a series of near equilibrium states, each stage being only infinitesimally removed from the equilibrium state. The path of a reversible process can be represented on a thermodynamic diagram, like a \( pv \), or \( pT \), or any other such diagram.

A process is irreversible if the system and all parts of its surroundings cannot be exactly restored to their respective initial states after the process has occurred. It is possible to restore an irreversible process to its initial states. However, were the system restored to its initial state, it would not be possible also to return the surroundings to the their initial states.
Example 5.3-1 Consider a 100 lb mass suspended 10 ft above Earth’s surface as shown in Figure E5.3-1a. This mass possess \( m(g/g_c)h = 1000 \text{ ft-lbf} \) of potential energy.

Note: \( m(g/g_c)h = (100 \text{ lb}) \left( \frac{32.2 \text{ ft/s}^2}{32.2 \text{ lb-ft/s}^2} \right) (10 \text{ ft}) = 1000 \text{ ft-lbf} \)

Consider several processes that return this mass to Earth’s surface. For each process determine:
(a) if the return process is reversible.
(b) the actual work performed.

Case 1: We cut the rope that suspends the mass.

The mass will crash to Earth’s surface. The process cannot be reversed by the application of a very small force in the opposite direction. The process is irreversible and spontaneous.

No work is done during this process. All of the 1000 ft-lbf potential energy originally possessed by the mass is converted to heat energy absorbed by the surroundings.

Case 2: The mass is suspended by a pulley arrangement as shown in Figure E5.3-1b with a locked latch.

When the latch is unlocked, the 100 lb mass will again crash to Earth’s surface. However, in this case the 10 lb mass will be raised 10 ft and therefore now possess 100 ft·lbf of potential energy. The process cannot be reversed by the application of a very small force in the opposite direction. The process is irreversible and spontaneous.

100 ft·lbf of work is done by the falling 100 lb mass doing work on the 10 lb mass. 900 ft·lbf of the 1000 ft·lbf potential energy originally possessed by the 100 lb mass is converted to heat energy absorbed by the surroundings.

**Case 2:** The mass is suspended by a pulley arrangement as shown in Figure E5.3-1c with a locked latch.

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**Figure E5.3-1b** 100 lb mass connected to a 10 lb mass by pulley/latch system.
When the latch is now unlocked the two 100 lb masses remain in the original position. They are in a state of equilibrium. This is not a spontaneous process. We now add a single grain of sand to the left-side mass. The suspended \((100 + dm)\) lb mass will slowly descend while raising the 100 lb mass from Earth’s surface. Eventually the 100 lb mass will be raised 10 ft and possess 1000 ft-lbf of potential energy. In this process, no heat is rejected to the surroundings. Moving the grain of send from the left-side mass to the right-side mass can reverse the process. The process is reversible.

5.4 Maximum Performance for Thermodynamic Cycles

All reversible power cycles operating between the same two thermal reservoirs have the same thermal efficiency. The thermal efficiency \(\eta\) of the power cycle is given by

\[
\eta = \frac{W_{\text{cycle}}}{Q_H} = \frac{Q_H - Q_C}{Q_C} = 1 - \frac{Q_C}{Q_H}
\]  

(5.4-1)

For a reversible power cycle, the ratio of the heat transfers \(\frac{Q_C}{Q_H}\) depends only on the reservoir temperatures. That is

\[
\left(\frac{Q_C}{Q_H}\right)_{\text{rev cycle}} = \psi(\theta_C, \theta_H)
\]

(5.4-2)

In this expression, \(\theta_C\) and \(\theta_H\) denote the temperature of the reservoir and the function \(\psi\) will need to be specified. Equation (5.4-2) provides a basis for defining a thermodynamic temperature scale independent of the properties of any substance. A simple choice for the function \(\psi\) is given by

\[
\left(\frac{Q_C}{Q_H}\right)_{\text{rev cycle}} = \frac{T_C}{T_H}
\]

(5.4-3)

Equation (5.4-3) defines the Kelvin temperature scale. The thermal efficiency of a system undergoing a reversible power cycle is then

\[
\eta = \frac{W_{\text{cycle}}}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}
\]

(5.4-4)

Equation (5.4-4) provides the thermal efficiency of all reversible power cycles operating between two reservoirs at temperatures \(T_H\) and \(T_C\). This thermal efficiency is the maximum efficiency any power cycle can have while operating between the two reservoirs at temperatures \(T_H\) and \(T_C\).
Example 5.4-1. An inventor claims to have developed a power cycle capable of delivering a net work output of 410 kJ for an energy input by heat transfer of 1000 kJ. The system undergoing the cycle receives the heat transfer from hot gases at a temperature of 500 K and discharges energy by heat transfer to the atmosphere at 300 K. Evaluate this claim.

Solution

The actual thermal efficiency claimed by the inventor is

\[ \eta = \frac{W_{\text{cycle}}}{Q_H} = \frac{410 \text{ kJ}}{1000 \text{ kJ}} = 0.41 \]

The maximum thermal efficiency for the power cycle operating between the two reservoirs at temperatures \( T_H = 500 \text{ K} \) and \( T_C = 300 \text{ K} \) is

\[ \eta = 1 - \frac{T_C}{T_H} = 1 - \frac{300 \text{ K}}{500 \text{ K}} = 0.40 \]

The claim is not valid since the actual thermal efficiency is higher than the maximum thermal efficiency.

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