THE SECOND LAW OF THERMODYNAMICS

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Summary.

Currently in the world exist several texts of Thermodynamic, which allow us the analysis of this science, that which becomes difficult in some occasions for the reader due language that is used in the texts. This work is an analysis of several texts for to carry out an approach to the student and to guide them toward the use of the English language.

We analyzed the second law of thermodynamics states, and it is exposed that processes occur in a certain direction, not in just any direction. Physical processes in nature can proceed toward equilibrium spontaneously. Once it has taken place, a spontaneous process can be reversed, but it will not reverse itself spontaneously.

When applied to processes, the second law also leads to the definition of a new property, known as *entropy*. If the first law is said to be the law of internal energy, the second law may be stated to be the law of entropy. At the end of this work we talk about the *exergy*, which is the useful work potential of the energy. Once the exergy is wasted, it can never be recovered.

Key words: Thermodynamics process, Second law, entropy, exergy.

INTRODUCTION

The second law of thermodynamics states that processes occur in a certain direction, not in just any direction. Physical processes in nature can proceed toward equilibrium spontaneously:

Water flows down a waterfall.

Gases expand from a high pressure to a low pressure.

Heat flows from a high temperature to a low temperature.

Once it has taken place, a spontaneous process can be reversed, but it will not reverse itself spontaneously. Some external inputs, energy, must be expended to reverse the process. As it falls down the waterfall, water can be collected in a water wheel, cause a shaft to rotate, coil a rope onto the shaft, and lift a weight. So the energy of the falling water is captured as potential energy increase in the weight, and the first law of thermodynamics is satisfied. However, there are losses associated with this process (friction). Allowing the weight to fall, causing the shaft to rotate in the opposite direction, will not pump all of the water back up the waterfall. Spontaneous processes can proceed only in a particular direction. The first law of thermodynamics gives no information about direction; it states only that when one form of energy is converted into another, identical quantities of energy are involved regardless of the feasibility of the process.

We know by experience that heat flows spontaneously from a high temperature to a low temperature. But heat flowing from a low temperature to a higher temperature with no expenditure of energy to cause the process to take place would not violate the first law.

The first law is concerned with the conversion of energy from one form to another. *Joule's experiments showed that energy in the form of heat could not be completely converted into work; however, work energy can be completely converted into heat energy.* Evidently heat and work are not completely interchangeable forms of energy. Furthermore, when energy is transferred from one form to another, there is often a degradation of the supplied energy into a less "useful" form. We shall see that it is the second law of thermodynamics that controls the direction processes may take and how much heat is converted into work.

A process will not occur unless it satisfies both the first and the second laws of thermodynamics.

To identify the direction of the process we will use a new property called entropy, a quantitative measure of microscopic disorder for a system. Entropy is a measure of energy that is no longer available to perform useful work within the current environment. Another important properties that win great importance with the global energy problem is the exergy, which is defined as the useful work potential of a system at the specified state. Once the exergy is wasted, it can never be recovered. When we use energy (to heat our homes, for example), we are not destroying any energy; we are merely converting it to a less useful form, a form of less exergy.

The Second Law of Thermodynamics

Some Definitions.

To express the second law in a workable form, we need the following definitions.

Heat (thermal) reservoir

A heat reservoir is a sufficiently large system in stable equilibrium to which and from which finite amounts of heat can be transferred without any change in its temperature.

A high temperature heat reservoir from which heat is transferred is sometimes called a heat source. A low temperature heat reservoir to which heat is transferred is sometimes called a heat sink.

Work reservoir

A work reservoir is a sufficiently large system in stable equilibrium to which and from which finite amounts of work can be transferred adiabatically without any change in its pressure.

Thermodynamic cycle.

A system has completed a thermodynamic cycle when the system undergoes a series of processes and then returns to its original state, so that the properties of the system at the end of the cycle are the same as at its beginning.

Heat Engine

A heat engine is a thermodynamic system operating in a thermodynamic cycle to which net heat is transferred and from which network is delivered.

The system, or working fluid, undergoes a series of processes that constitute the heat engine cycle.

Thermal Efficiency, nth

The thermal efficiency is the index of performance of a work-producing device or a heat engine and is defined by the ratio of the network output (the desired result) to the heat input (the costs to obtain the desired result).

$$\eta_{th} = \frac{\text{Desired Result}}{\text{Required Input}}$$

For a heat engine the desired result is the net work done and the input is the heat supplied to make the cycle operate. *The thermal efficiency is always less than 1 or less than 100 percent*.

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}}$$

where

$$W_{\rm net,\,out} = W_{\rm out} - W_{\rm in}$$

Here the use of the *in* and *out* subscripts means to use the magnitude (take the positive value) of either the work or heat transfer and let the minus sign in the net expression take care of the direction.

Now apply the first law to the cyclic heat engine.

$$Q_{net, in} - W_{net, out} = \Delta U^{\bullet 0 (Cyclic)}$$

 $W_{net, out} = Q_{net, in}$

$$W_{net,out} = Q_{in} - Q_{out}$$

The cycle thermal efficiency may be written as

$$\eta_{th} = \frac{W_{net, out}}{Q_{in}} \qquad = \frac{Q_{in} - Q_{out}}{Q_{in}} \qquad = 1 - \frac{Q_{out}}{Q_{in}}$$

Heat Pump and Refrigerator

A <u>heat pump</u> is a thermodynamic system operating in a thermodynamic cycle that removes heat from a low-temperature body and delivers heat to a high-temperature body. To accomplish this energy transfer, the heat pump receives external energy in the form of work or heat from the surroundings.

While the name "*heat pump*" is the thermodynamic term used to describe a cyclic device that allows the transfer of heat energy from a low temperature to a higher temperature, we use the terms "*refrigerator*" and "*heat pump*" to apply to particular devices. Here a refrigerator is a device that operates on a thermodynamic cycle and extracts heat from a low-temperature medium. The heat pump also operates on a thermodynamic cycle but rejects heat to the high-temperature medium.

Coefficient of Performance, COP.

The index of performance of a refrigerator or heat pump is expressed in terms of the coefficient of performance, **COP**, the ratio of desired result to input. This measure of performance may be larger than 1, and we want the COP to be as large as possible.

 $COP = \frac{\text{Desired Result}}{\text{Required Input}}$

For the heat pump acting like a refrigerator or an air conditioner, the primary function of the device is the transfer of heat *from* the low temperature system.

For the refrigerator the desired result is the heat supplied at the low temperature and the input is the net work into the device to make the cycle operate.

$$COP_{R} = \frac{Q_{L}}{W_{net, in}}$$

Now apply the first law to the cyclic refrigerator.

$$(Q_L - Q_H) - (0 - W_{in}) = \Delta U_{cycle} = 0$$
$$W_{in} = W_{net, in} = Q_H - Q_L$$

and the coefficient of performance becomes

$$COP_{R} = \frac{Q_{L}}{Q_{H} - Q_{L}}$$

For the device acting like a "heat pump," the primary function of the device is the transfer of heat to the high-temperature system. The coefficient of performance for a heat pump is

$$COP_{HP} = \frac{Q_H}{W_{net, in}} = \frac{Q_H}{Q_H - Q_L}$$

Note, under the same operating conditions the $\ensuremath{\text{COP}_{\text{HP}}}$ and $\ensuremath{\text{COP}_{\text{R}}}$ are related by

$$COP_{HP} = COP_{R} + 1$$

Second Law Statements.

The following two statements of the second law of thermodynamics are based on the definitions of the heat engines and heat pumps.

Kelvin-Planck statement of the second law

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.

The Kelvin-Planck statement of the second law of thermodynamics states that no heat engine can produce a net amount of work while exchanging heat with a single reservoir only. In other words, the maximum possible efficiency is less than 100 percent.



Figure 1.1: Kelvin-Planck statement demonstration (Heat engine that violates the Kelvin-Planck statement of the second law)

Clausius statement of the second law.

The Clausius statement of the second law states that 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.



Figure 1.2: Clausius statement demonstration (Heat pump that violates the Clausius statement of the second law)

A violation of either the Kelvin-Planck or Clausius statements of the second law implies a violation of the other. Assume that the heat engine shown below is violating the Kelvin-Planck statement by absorbing heat from a single reservoir and producing an equal amount of work W. The output of the engine drives a heat pump that transfers an amount of heat QL from the low-temperature thermal reservoir and an amount of heat QH + QLto the high-temperature thermal reservoir. The combination of the heat engine and refrigerator in the left figure acts like a heat pump that transfers heat QL from the lowtemperature reservoir without any external energy input. This is a violation of the Clausius statement of the second law.



Figure 1.3a: A refrigerator which is powered by a 100 % efficient heat engine Figure 1.3b: The equivalent refrigerator

1.3a)

1.3b)

Perpetual-Motion Machines.

Any device that violates the first or second law of thermodynamics is called a perpetualmotion machine. If the device violates the first law, it is a perpetual-motion machine of the first kind. If the device violates the second law, it is a perpetual-motion machine of the second kind.

Reversible Processes.

A reversible process is a quasi-equilibrium, or quasi-static, process with a more restrictive requirement.

Internally reversible process.

The internally reversible process is a quasi-equilibrium process, which, once having taken place, can be reversed and in so doing leave no change in the system. This says nothing about what happens to the surroundings about the system.

Totally or externally reversible process.

The externally reversible process is a quasi-equilibrium process, which, once having taken place, can be reversed and in so doing leave no change in the system or surroundings.

Irreversible Process.

An irreversible process is a process that is not reversible. All real processes are irreversible. Irreversible processes occur because of the following: Friction Unrestrained expansion of gases Heat transfer through a finite temperature difference Mixing of two different substances Hysteresis effects I^2R losses in electrical circuits Any deviation from a quasi-static process

The Carnot Cycle

French military engineer Nicolas Sadi Carnot (1769-1832) was among the first to study the principles of the second law of thermodynamics. Carnot was the first to introduce the concept of cyclic operation and devised a reversible cycle that is composed of four reversible processes, two isothermal and two adiabatic.

The Carnot Cycle

<u>Process 1-2</u>: Reversible isothermal heat addition at high temperature, $T_H > T_L$, to the working fluid in a piston-cylinder device that does some boundary work.

<u>Process 2-3</u>: Reversible adiabatic expansion during which the system does work as the working fluid temperature decreases from T_H to T_L .

<u>Process 3-4</u>: The system is brought in contact with a heat reservoir at $T_L < T_H$ and a reversible isothermal heat exchange takes place while work of compression is done on the system.

<u>Process 4-1</u>: A reversible adiabatic compression process increases the working fluid temperature from T_L to T_{H} .



Figure 1.4: P-v diagram, Carnot Cycle

You may have observed that power cycles operate in the clockwise direction when plotted on a process diagram. The Carnot cycle may be reversed, in which it operates as a refrigerator. The refrigeration cycle operates in the counterclockwise direction.



Figure 1.5: *P-v* diagram, Reversed Carnot Cycle

Carnot Principles

The second law of thermodynamics puts limits on the operation of cyclic devices as expressed by the Kelvin-Planck and Clausius statements. A heat engine cannot operate by exchanging heat with a single heat reservoir, and a refrigerator cannot operate without net work input from an external source.

Consider heat engines operating between two fixed temperature reservoirs at TH > TL. We draw two conclusions about the thermal efficiency of reversible and irreversible heat engines, known as the Carnot principles.

(a) The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.

$$\eta_{{}_{th}}$$
 < $\eta_{{}_{th}, Carnot}$

(b) The efficiencies of all reversible heat engines operating between the same two constant-temperature heat reservoirs have the same efficiency.

Since the thermal efficiency in general is

$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

This is the maximum possible efficiency of a heat engine operating between two heat reservoirs at temperatures T_H and T_L . Note that the temperatures are absolute temperatures.

These statements form the basis for establishing an absolute temperature scale, also called the Kelvin scale, related to the heat transfers between a reversible device and the high- and low-temperature heat reservoirs by

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

Then the Q_H/Q_L ratio can be replaced by *TH/TL* for reversible devices, where *TH* and *TL* are the absolute temperatures of the high- and low temperature heat reservoirs, respectively. This result is only valid for heat exchange across a heat engine operating between two constant temperature heat reservoirs. These results do not apply when the heat exchange is occurring with heat sources and sinks that do not have constant temperature.

The thermal efficiencies of actual and reversible heat engines operating between the same temperature limits compare as follows:

$$\eta_{th} \begin{cases} < \eta_{th, rev} & \text{irreversible heat engine} \\ = \eta_{th, rev} & \text{reversible heat engine} \\ > \eta_{th, rev} & \text{impossible heat engine} \end{cases}$$

Reversed Carnot Device Coefficient of Performance

If the Carnot device is caused to operate in the reversed cycle, the reversible heat pump is created. The COP of reversible refrigerators and heat pumps are given in a similar manner to that of the Carnot heat engine as

$$COP_{R} = \frac{Q_{L}}{Q_{H} - Q_{L}} = \frac{1}{\frac{Q_{H}}{Q_{L}} - 1} \qquad \qquad = \frac{T_{L}}{T_{H} - T_{L}} = \frac{1}{\frac{T_{H}}{T_{L}} - 1}$$
$$COP_{HP} = \frac{Q_{H}}{Q_{H} - Q_{L}} = \frac{\frac{Q_{H}}{Q_{L}}}{\frac{Q_{H}}{Q_{L}} - 1} \qquad \qquad = \frac{T_{H}}{T_{H} - T_{L}} = \frac{\frac{T_{H}}{T_{L}}}{\frac{T_{H}}{T_{L}} - 1}$$

Again, these are the maximum possible COPs for a refrigerator or a heat pump operating between the temperature limits of T_H and T_L .

The coefficients of performance of actual and reversible (such as Carnot) refrigerators operating between the same temperature limits compare as follows:

$$COP_{R} \begin{cases} < COP_{R, rev} & \text{irreversible refrigerator} \\ = COP_{R, rev} & \text{reversible refrigerator} \\ > COP_{R, rev} & \text{impossible refrigerator} \end{cases}$$

A similar relation can be obtained for heat pumps by replacing all values of COP_R by COP_{HP} in the above relation.

Entropy, a measure of disorder.

The fist law of thermodynamics was stated in terms of cycles first and it was show that the cyclic integral of heat is equal to the cyclic integral of work. When the first law was applied for thermodynamics process, the existence of a property, the internal energy, was found. Similarly, the second law was also first stated in terms of cycles executed by systems. When applied to processes, the second law also leads to the definition of a new property, known as *entropy*. *If the first law is said to be the law of internal energy, the second law may be stated to be the law of entropy*.

Entropy and the Clausius Inequality

The second law of thermodynamics leads to the definition of a new property called entropy, a quantitative measure of microscopic disorder for a system. Entropy is a measure of energy that is no longer available to perform useful work within the current environment.

Clausius' Theorem

Let smooth closed curve representing a reversible cycle (fig.6.1) be considered. Let the closed cycle be divided into a large number of strips by means of reversible adiabatics. Each strip may be closed at the top and bottom by reversible isotherms. The original closed cycle is thus replaced by a zig-zag closed path consisting of alternate adiabatic and isothermal processes, such that the heat transferred during all the isothermal processes is equal to the heat transferred in the original cycle. Thus the original cycle is replaced by a large number of Carnot cycles. If the adiabatics are close to one another and the number of Carnot cycle is large, the saw- toothed zig-zag line will coincide with the original cycle.



Figure 1.6: A reversible Split into a large number of Carnot Cycles.

For the elemental cycle abcd dQ_1 heat is absorbed reversibly at T_1 , and dQ_2 heat is rejected reversibly at T_2 .

$$\frac{dQ_1}{T_1} = \frac{dQ_2}{T_2}$$

If heat supplied is taken as positive and heat rejected as negative

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0$$

Similarly, for the elemental cycle efgh

$$\frac{dQ_3}{T_3} + \frac{dQ_4}{T_4} = 0$$

If similar equations are written for all elemental Carnot cycles, then for the whole original cycle.

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$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} + \frac{dQ_3}{T_3} + \frac{dQ_4}{T_4} + \dots = 0 \qquad \oint_R \frac{dQ}{T} = 0$$

The cycle integral of dQ/T for a reversible cycle is equal to zero. This is known as Clausius' theorem. The letter *R* emphasizes the fact that the equation is valid only for reversible cycle.

To obtain the working definition of entropy and, thus, the second law, let's derive the Clausius inequality.

The Inequality of Clausius

Let us consider a cycle *ABCD* (fig. 6.2). Let *AB* be general process, either reversible or irreversible, while the other process in the cycle are reversible. Let the cycle be divided into a number of elementary cycles, as shown. For one of these elementary cycles

$$\eta = 1 - \frac{dQ_2}{dQ}$$

Where dQ is the heat supplied a *T*, and dQ_2 the heat rejected at T_2 .



Figure 1.7: Inequality of Clausius

Now the efficiency of general cycle will be equal to less than the efficiency of a reversible cycle.

$$1 - \frac{dQ_2}{dQ} \le \left(1 - \frac{dQ_2}{dQ}\right)_{rev}$$
$$\frac{dQ_2}{dQ} \ge \left(\frac{dQ_2}{dQ}\right)_{rev}$$
$$\frac{dQ}{dQ_2} \le \left(\frac{dQ}{dQ_2}\right)_{rev}$$
$$\left(\frac{dQ}{dQ_2}\right)_{rev} = \frac{T}{T_2}$$
$$\frac{dQ}{dQ_2} \le \frac{T}{T_2}$$

or $dQ / T \le dQ_2 / T_2$, for any process AB, reversible or irreversible.

For reversible process

$$ds = \frac{dQ_{rev}}{T} = \frac{dQ_2}{T_2}$$

Hence for any process AB

$$\frac{dQ}{T} \le ds$$

Then for any cycle

$$\oint \frac{dQ}{T} \le \oint ds$$

Since entropy is a property and the cyclic integral of any property is cero

$$\oint \frac{dQ}{T} \le 0$$

This equation is known as the *inequality of Clausius*. It provides the criterion of the reversible cycle.

If

$$\oint \frac{dQ}{T} = 0$$
 The cycle is reversible.
$$\oint \frac{dQ}{T} < 0$$
 The cycle is irreversible and possible.
$$\oint \frac{dQ}{T} > 0$$
, the cycle is impossible, since it violates the second law.

Example 1

For a particular power plant, the heat added and rejected both occurs at constant temperature and no other processes experience any heat transfer. The heat is added in the amount of 3150 kJ at 440oC and is rejected in the amount of 1950 kJ at 20 0C. Is the Clausius inequality satisfied and is the cycle reversible or irreversible?

$$\oint \frac{\delta Q_{net}}{T} \leq 0 \qquad \int \left(\frac{\delta Q_{net}}{T}\right)_{in} + \int \left(\frac{\delta Q_{net}}{T}\right)_{out} \leq 0$$

$$\left(\frac{Q_{net}}{T}\right)_{in} + \left(\frac{Q_{net}}{T}\right)_{out} \leq 0 \qquad \left(\frac{Q_{in}}{T_{in}}\right) + \left(\frac{-Q_{out}}{T_{out}}\right) \leq 0$$

$$\left(\frac{3150 \, kJ}{(440 + 273)K}\right) + \left(\frac{-1950 \, kJ}{(20 + 273)K}\right) \leq 0$$

$$(4.418 - 6.655) \frac{kJ}{K} \leq 0 \qquad -2.237 \frac{kJ}{K} \leq 0$$

Calculate the net work, cycle efficiency, and Carnot efficiency based on *TH* and *TL* for this cycle.

$$\begin{split} W_{net} &= Q_{in} - Q_{out} = (3150 - 1950) \, kJ = 1200 \, kJ \\ \eta_{th} &= \frac{W_{net}}{Q_{in}} = \frac{1200 \, kJ}{3150 \, kJ} = 0.381 \ or \ 38.1\% \\ \eta_{th,Carnot} &= 1 - \frac{T_L}{T_H} = 1 - \frac{(20 + 273) \, K}{(440 + 273) \, K} = 0.589 \ or \ 58.9\% \end{split}$$

The Clausius inequality is satisfied. Since the inequality is less than zero, the cycle has at least one irreversible process and the cycle is irreversible.

Definition of Entropy

Let's take another look at the quantity

$$\oint \frac{\delta Q_{net}}{T} \le 0$$

If no irreversibilities occur within the system as well as the reversible cyclic device, then the cycle undergone by the combined system will be internally reversible. As such, it can be reversed. In the reversed cycle case, all the quantities will have the same magnitude but the opposite sign. Therefore, the work W_C , which could not be a positive quantity the regular case, cannot be a negative quantity in the reversed case. Then it follows that $W_{C,intrev} = 0$ since it cannot be a positive or negative quantity, and therefore

$$\oint \left(\frac{\delta Q_{net}}{T}\right)_{\text{int rev}} = 0$$

for internally reversible cycles. Thus we conclude that the equality in the Clausius inequality holds for totally or just internally reversible cycles and the inequality for the irreversible ones.

Example 2

Consider the cycle shown below composed of two reversible processes A and B. Apply the Clausius inequality for this cycle. What do you conclude about these two integrals?



A cycle composed of two reversible processes.



Apply the Clausius inequality for the cycle made of two internally reversible processes:

$$\oint \left(\frac{\delta Q_{net}}{T}\right)_{int rev} = 0$$

You should find:
$$\underbrace{\int_{1}^{2} \left(\frac{\delta Q_{net}}{T}\right)_{int rev}}_{along path A} = \underbrace{\int_{1}^{2} \left(\frac{\delta Q_{net}}{T}\right)_{int rev}}_{along path B}$$

Since the quantity (**\delta Qnet/T**) int.rev is independent of the path and must be a property, we call this property the **entropy** *S*.

The entropy change occurring during a process is related to the heat transfer and the temperature of the system. The entropy is given the symbol S (kJ/K), and the specific entropy is s (kJ/kg K).

The entropy change during a reversible process, sometimes called an internally reversible process, is defined as

$$dS = \frac{\delta Q_{net}}{T}\Big|_{\text{intrev}} \qquad \qquad S_2 - S_1 = \int_1^2 \frac{\delta Q_{net}}{T}\Big|_{\text{intrev}}$$

Consider the cycle 1-A-2-B-1, shown below, where process A is arbitrary that is, it can be either reversible or irreversible, and process B is internally reversible.



A cycle composed of reversible and irreversible processes.

$$\oint \left(\frac{\delta Q_{net}}{T}\right)_{\text{int rev}} \le 0 \qquad \qquad \underbrace{\int_{1}^{2} \frac{\delta Q_{net}}{T}}_{along A} + \underbrace{\int_{2}^{1} \left(\frac{\delta Q_{net}}{T}\right)_{\text{int rev}}}_{along B} \le 0$$

.

The integral along the internally reversible path, process B, is the entropy change S1 - S2. Therefore,

$$\int_{1}^{2} \frac{\delta Q_{net}}{T} + S_1 - S_2 \leq 0$$

or

$$S_2 - S_1 \ge \int_1^2 \frac{\delta Q_{net}}{T}$$

In general the entropy change during a process is defined as

$$dS \ge \frac{\delta Q_{net}}{T}$$
 where = holds for the internally reversible process > holds for the irreversible process

Consider the effect of heat transfer on entropy for the internally reversible case.

$$dS = \frac{\delta Q_{net}}{T}$$

Being *T* the thermodynamic temperature to which it is emitted or receives the heat

Which temperature *T* is this one? If

$$\begin{split} &\delta Q_{net} > 0, & then \ dS > 0 \\ &\delta Q_{net} = 0, & then \ dS = 0 \\ &\delta Q_{net} < 0, & then \ dS < 0 \end{split}$$

This last result shows why we have kept the subscript **net** on the heat transfer Q. It is important for you to recognize that Q has a sign depending on the direction of heat transfer. The **net** subscript is to remind us that Q is positive when added to a system and negative when leaving a system. Thus, the entropy change of the system will have the same sign as the heat transfer in a reversible process.

From the above, we see that for a reversible, adiabatic process

$$dS = 0 \qquad S_2 = S_1$$

The reversible, adiabatic process is called an isentropic process.

Entropy change is caused by heat transfer and irreversibilities. Heat transfer to a system increases the entropy; heat transfer from a system decreases it. The effect of irreversibilities is always to increase the entropy. In fact, a process in which the heat

transfer is out of the system may be so irreversible that the actual entropy change is positive. Friction is one source of irreversibilities in a system.

The entropy change during a process is obtained by integrating the *dS* equation over the process:

Here, the inequality is to remind us that the entropy change of a system during an irreversible process is always greater than $\int_{1}^{2} \delta Q / T$ called the entropy transfer.

$$\Delta S_{sys} = S_2 - S_1 \ge \int_1^2 \frac{\delta Q_{net}}{T} \qquad \left(\frac{kJ}{K}\right)$$

Definition of Second Law of Thermodynamics.

Now consider an isolated system composed of several subsystems exchanging energy among them selves. Since the isolated system has no energy transfer across its system boundary, the heat transfer across the system boundary is zero.



Figure 1.8 The entropy change of an isolated system is the sum of the entropy changes of its components, and is never less than zero.

Applying the definition of entropy to the isolated system

$$\Delta S_{isolated} \ge \int_{1}^{2} \frac{\delta Q_{net}}{T}^{0, \text{ adiabatic}}$$

The total entropy change for the isolated system is

$$\Delta S_{isolated} \ge 0$$

This equation is the working definition of the second law of thermodynamics. The second law, known as the principle of increase of entropy, is stated as

The total entropy change of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant.

Now consider a general system exchanging mass as well as energy with its surroundings.



$$S_{gen} = \Delta S_{total} = \Delta S_{sys} + \sum \Delta S_{surr} \ge 0$$

where

= holds for the totally reversible process > holds for the irreversible process

Figure 1.9:A system and its surroundings form an isolated system.

Thus, the entropy generated or the total entropy change (sometimes called the entropy change of the universe or net entropy change) due to the process of this isolated system is positive (for actual processes) or zero (for reversible processes). The total entropy change for a process is the amount of entropy generated during that process (**Sgen**), and it is equal to the sum of the entropy changes of the system and the surroundings. The entropy changes of the important system (closed system or control volume) and its surroundings do not both have to be positive. The entropy for a given system (important or surroundings) may decrease during a process, **but the sum of the entropy changes of the system and its surroundings for an isolated system can never decrease**.

Entropy change is caused by heat transfer and irreversibilities. Heat transfer to a system increases the entropy, and heat transfer from a system decreases it. The effect of irreversibilities is always to increase the entropy.

The increase in entropy principle can be summarized as follows:

$$S_{gen} = \Delta S_{Total} \begin{cases} > 0 & \text{Irreversible processes} \\ = 0 & \text{Reversible processes} \\ < 0 & \text{Impossible processes} \end{cases}$$

Some Remarks about Entropy

- 1. Processes can occur in a certain direction only, not in just any direction, such that $Sgen \ge 0$.
- 2. Entropy is a nonconserved property, and there is no such thing as the conservation of entropy principle. The entropy of the universe is continuously increasing.
- 3. The performance of engineering systems is degraded by the presence of irreversibilities, and entropy generation is a measure of the magnitudes of the irreversibilities present during that process.

Isothermal, Reversible Process

For an isothermal, reversible process, the temperature is constant and the integral to find the entropy change is readily performed. If the system has a constant temperature, T_0 , the entropy change becomes

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta Q_{net}}{T} = \frac{Q_{net}}{T_o}$$

For a process occurring over a varying temperature, the entropy change must be found by integration over the process.

Adiabatic, Reversible (Isentropic) Process

For an adiabatic process, one in which there is no heat transfer, the entropy change is

$$\Delta S = S_2 - S_1 \ge \int_1^2 \frac{\delta Q_{net}}{T}$$
0, adiabatic
$$\Delta S = S_2 - S_1 \ge 0$$

If the process is adiabatic and reversible, the equality holds and the entropy change is

$$\Delta S = S_2 - S_1 = 0$$
$$S_2 = S_1$$

or on a per unit mass basis

$$s = \frac{S}{m} \qquad S_2 = S_1$$

The adiabatic, reversible process is a constant entropy process and is called isentropic.

The effect of decreasing the ΔT for heat transfer is to reduce the entropy generation or total entropy change of the universe due to the isolated system and the irreversibilities associated with the heat transfer process.

Exergy. A Measure of Work Potential

The energy content of the universe is constant, just as its mass content is. Yet at times of crisis we are bombarded with speeches and articles on how to "conserve" energy. As engineers, we know that energy is already conserved. What is not conserved is *exergy*, which is the useful work potential of the energy. Once the exergy is wasted, it can never be recovered. When we use energy (to heat our homes, for example), we are not destroying any energy; we are merely converting it to a less useful form, a form of less exergy.

Exergy and the Dead State

The useful work potential of a system at the specified state is called **exergy or available** energy. The exergy is a property and is associated with the state of the system and the environment. A system that is in equilibrium with its surroundings has zero exergy and is said to be at the *dead state*. The properties of a system at the dead state are denoted by subscript zero, for example *Po*, *To*, *Ho*, *Uo*, $(To=25 \ ^{o}C \ and \ Po=1 \ atm.)$. The exergy of the thermal energy of thermal reservoirs is equivalent to the work output of a Carnot heat engine operating between the reservoir and the environment.

Reversible Work

Reversible work (*W*rev) is defined as the maximum amount of useful work that can be produced (or the minimum work that needs to be supplied) as a system undergoes a process between the specified initial and final states. This is the useful work output (or input) obtained when the process between the initial and final states is executed in a totally reversible manner.

Irreversibility

The difference between the reversible work (Wrev) and the useful work (Wu) is due to the irreversibilities present during the process and is called the *irreversibility* (I). It is equivalent to the *exergy destroyed* and is expressed as

$$I = X_{\textit{destroyed}} = T_o S_{\textit{gen}} = W_{\textit{rev,out}} - W_{u,\textit{out}} = W_{u,\textit{in}} - W_{\textit{rev,in}}$$

where **Sgen** is the entropy generated during the process. For a totally reversible process, the useful and reversible work terms are identical and thus irreversibility is zero. *Exergy destroyed* represents the lost work potential and is also called the *wasted work* or *lost work*.

Second-Law Efficiency

The *second-law efficiency* is a measure of the performance of a device relative to the performance under reversible conditions for the same end states and is given by:

$$\eta_{II} = \frac{\eta_{th}}{\eta_{th,rev}} = \frac{W_u}{W_{rev}}$$

for heat engines and other work-producing devices.

We can also define a second-law efficiency for work consuming non-cyclic (such as compressor) a cyclic (such as refrigerators) devices as the ratio of the minimum (reversible)work input to the useful work imput

$$\eta_{II} = \frac{COP}{COP_{rev}} = \frac{W_{rev}}{W_u}$$

In general, the second-law efficiency is expressed as

$$\eta_{II} = \frac{\text{Exergy recovered}}{\text{Exergy supplied}} = 1 - \frac{\text{Exergy destroyed}}{\text{Exergy supplied}}$$

Exergy Forms

Now let's determine the exergy of various forms of energy.

Exergy of kinetic energy

Kinetic energy is a form of mechanical energy and can be converted directly into work. Kinetic energy itself is the work potential or exergy of kinetic energy independent of the temperature and pressure of the environment.

Exergy of kinetic energy:
$$x_{ke} = ke = \frac{\vec{V}^2}{2}$$

Exergy of potential energy

Potential energy is a form of mechanical energy and can be converted directly into work. Potential energy itself is the work potential or exergy of potential energy independent of the temperature and pressure of the environment.

Exergy of potential energy:
$$x_{pe} = pe = gz$$

Exergy of a fixed mass (Closed System) (X_u) .

The exergy of a fixed mass (nonflow exergy) is expressed as the sum of the exergies of its internal energy, kinetic energy, and potential energy.

$$x_{nonflow} = x_u + x_{ke} + x_{pe}$$

Neglect the kinetic energy, and potential energy for closed system $\Delta KE=0$, $\Delta PE=0$. The exergy of a fixed mass only depend of the exergises of its internal energy.

$$x_{nonflow} = x_u$$

Applied the first law of thermodynamics in the figure below (for reversible process, 1-0)



Figure 1.10: Piston device (Applied the first law of thermodynamics)

The work done by the device is not always totally usable

Example

When a gas in piston- cylinder devices expands, part of the work done by the gas is used to push the atmospheric air out of the way of the piston. This work, which cannot be recovered and utilized for any useful propose, is equal to the atmospheric pressure, P_o times the volume change of the system.

$$W_{surr} = P_o(V_0 - V_1)$$

The difference between the actual work $(W_{(1-0)})$ and the surrounding work (W_{surr}) is called the total useful work $(W_{T.useful})$.

$$W_{T.useful} = W_{(1-0)} - W_{(surr)}$$
$$W_{T.useful} = -Q - \Delta U - W_{(surr)}$$
$$W_{T.useful} = (U_1 - U_0) - P_0 \cdot (V_0 - V_1) - Q$$

When we apply the principle of increase of entropy

$$\Delta S_{iso,sys} \ge 0$$

Note:

The equality holds for reversible process, when we have the reversible process, the work realized for the system is the must height possible.

$$\Delta S_{iso,sys} = \Delta S_{sys} + \Delta S_{surr} \ge 0$$

Considering Reversible process

$$\Delta S_{iso,sys} = 0$$

then

$$\Delta S_{surr} = -\Delta S_{sys}$$

where $\Delta S_{surr} = \frac{Q}{T_0}$

$$\Delta S_{sys} = (S_o - S_1)$$

The equation become in

$$\frac{Q}{T_0} = (S_1 - S_0)$$
$$Q = (S_1 - S_0)T_0$$

The useful work it is equal:

$$W_{T.useful} = (U_1 - U_0) - P_0 \cdot (V_0 - V_1) - (S_1 - S_0)T_0$$

The $W_{t.useful}$ is the total useful work delivered as the system undergoes a reversible process from the given state to the dead state, which is the exergy by definition.

Exergy for closed system(X_u) or exergy for internal energy.

$$X_{u} = (U_{1} - U_{0}) - P_{0} \cdot (V_{0} - V_{1}) - (S_{1} - S_{0})T_{0}$$
 (kJ).

Exergy per unit mass

$$x_u = (u_1 - u_0) - P_0 \cdot (v_0 - v_1) - (s_1 - s_0)T_0 \quad (kJ/kg).$$

Exergy of flow work

The energy needed to force mass to flow into or out of a control volume is the flow work per unit mass given by



Figure 1.11: The exergy of flow work is the useful work that would be delivered by an imaginary piston in the flow section

The exergy of flow work is the excess of flow work done against atmospheric air at P_0 to displace it by volume v. According to the above figure, the useful work potential due to flow work is

$$W_{flow, useful} = Pv - P_o v$$

Thus, the exergy of flow work is

Exergy of flow work:
$$x_{pv} = Pv - P_o v = (P - P_o)v$$

Exergy of enthalpy (X_h)

Since enthalpy is the sum of internal energy and the flow work, the exergy of enthalpy is the sum of the exergies of internal energy and flow work

$$\begin{aligned} x_h &= x_u + x_{pv} \\ &= (u - u_o) + P_o(v - v_o) - T_o(s - s_o) + (P - P_o)v \\ &= (u - u_o) + P(v - v_o) - T_o(s - s_o) \\ &= (h - h_0) - T_0(s - s_0) \end{aligned}$$

Exergy of enthalpy:

$$x_h = (h - h_o) - T_o(s - s_o)$$
 kJ/kg

The exergy of enthalpy can be negative if the pressure is lower than atmospheric pressure.

Exergy Change of a Flow Stream (Open System), (X_{Flow}) or (Ψ) .

The exergy of a flow stream is expressed as the sum of the exergies of its enthalpy energy, kinetic energy, and potential energy.

$$x_{flow} = x_h + x_{ke} + x_{pe}$$

This is called the flow (or open system) exergy ψ and is given on a unit mass basis as

Flow exergy:

$$\psi = (h - h_o) - T_o(s - s_o) + \frac{\vec{V}^2}{2} + gz \qquad kJ/kg$$

Exergy Transfer by Heat, Work, and Mass

Exergy can be transferred by heat, work, and mass flow, and exergy transfer accompanied by heat, work, and mass transfer are given by the following.

Exergy transfer by heat transfer

By the second law we know that only a portion of heat transfer at a temperature above the environment temperature can be converted into work. The maximum useful work is produced from it by passing this heat transfer through a reversible heat engine. The exergy transfer by heat is

Exergy transfer by heat:
$$X_{heat} = \left(1 - \frac{T_o}{T}\right)Q$$

Note that exergy transfer by heat is zero for adiabatic systems.

Exergy transfer by work

Exergy is the useful work potential, and the exergy transfer by work can simply be expressed as

Exergy transfer by work: $X_{work} = \begin{cases} W - W_{surr} & \text{(for boundary work)} \\ W & \text{(for other forms of work)} \end{cases}$

where $W_{\text{surrev}} = P_0 (V_2 - V_1) P_0$ is atmospheric pressure, and V_1 and V_2 are the initial and final volumes of the system. The exergy transfer for shaft work and electrical work is equal to the work W itself.

Exergy transfer by mass

Mass flow is a mechanism to transport exergy, entropy, and energy into or out of a system. As mass in the amount m enters or leaves a system the exergy transfer is given by

Exergy transfer by mass:
$$X_{mass} = m\psi$$

The Decrease of Exergy Principle and Exergy Destruction

The exergy of an isolated system during a process always decreases or, in the limiting case of a reversible process, remains constant. This is known as the *decrease of exergy principle* and is expressed as

$$\Delta X_{isolated} = (X_2 - X_1)_{isolated} \le 0$$

Exergy Destruction.(X_{dest}) or (S_{dest})

Irreversibilities such as friction, mixing, chemical reactions, and heat transfer through finite temperature difference, unrestrained expansion, non quasiequilibrium compression, or expansion always generate entropy, and anything that generates entropy always destroys exergy. The exergy destroyed is proportional to the entropy generated as expressed as

$$X_{destroyed} = T_o S_{gen}$$

The decrease of exergy principle does not imply that the exergy of a system cannot increase. The exergy change of a system can be positive or negative during a process, but exergy destroyed cannot be negative. The decrease of exergy principle can be summarized as follows:

$$X_{destroyed}$$
 $\begin{cases} > 0 & Irreversible proces \\ = 0 & Reversible process \\ < 0 & Impossible process \end{cases}$

Other form to express the exergy destroyed is to make the exergy balance.

The exergy balance: Is the exergy change of a system during a process is equal to the difference between the net exergy entering in the system plus the exergy at the beginning of the system, and the exergy at the final process plus the exergy produce in the process.

Destroyed exergy for closed system (X_{dest}) .

$$X_{dest} = (X_1 + X_{heat}) - X_2 \pm X_{w.useful}$$

$$X_{dest} = (U_1 - U_2) - T_0(S_1 - S_2) + P_0(V_1 - V_2) + (1 - \frac{T_0}{T_{high}})Q \pm X_{w.useful}$$

Note:

When the work is done on the system the $X_{w.useful}$ it is (+).

When the work is done by the system the $X_{w.useful}$ it is (--).

Per unit mass

$$x_{dest} = (u_1 - u_2) - T_0(s_1 - s_2) + P_0(v_1 - v_2) + (1 - \frac{T_0}{T_{high}})q \pm x_{w.useful} \quad (kJ/Kg)$$

Destroyed exergy for Open–System (X $_{dest}$) or (S $_{dest}$).

$$X_{dest} = (X_1 + X_{heat}) - X_2 \pm X_{w.useful}$$

Per unit mass.

$$x_{dest} = (x_1 + x_{heat}) - x_2 \pm x_{w.useful}$$

General expression

$$x_{dest} = \sum_{in} x - \sum_{out} x \pm x_{w.useful}$$
 (kJ/kg)

Simple case.

$$x_{dest} = (h_1 - h_2) - T_0(s_1 - s_2) + (1 - \frac{T_0}{T_{high}})q \pm x_{w.useful}$$

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Conclusions.

At the end of this work, it can concluded that the second law of the thermodynamics is one of the most important laws in the thermodynamics. This allows us to determine when a process is possible or not and in what way it can happen. This can be determine when works is done with the total entropy change of an isolated system during a process, in which the entropy always increase. It can also be define that the exergy is one of the most useful properties in modern Thermoenergetics, since it allows us to determine how a system can be made the most efficient way possible, by destroying the smallest amount of exergy possible.

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