

The Second Law of Thermodynamics

As we have learned, mechanical energy and heat are only different forms of energy, but while mechanical energy can be completely converted to heat by such processes as friction, it is impossible to convert heat completely to work. Even by using reversible engines which are the most efficient, only a fraction can be converted to work. The conversion is therefore only partial.

It is fact of experience that *no heat engine has ever been developed that converts the heat extracted from a heat reservoir into work without rejecting some heat to a heat sink*. This negative statement, which is the result of everyday experience, constitute ***Kelvin-Planck statement of the second law of thermodynamics***.

This is also an experience, *that work is always necessary to transfer heat from a reservoir at low temperature (sink) to a (heat) reservoir at high temperature*, because it is a fact of nature that *heat does not flow spontaneously from low temperature to high temperature reservoir*. This negative statement leads us to the ***Clausius statement of the second law of thermodynamics***.

Equivalence of The Kelvin-Planck's and Clausius' Statement

The two statements of second law of thermodynamics are just two different ways of explaining the same problem, i.e., the two statements are equivalent. In other words, the violation of Kelvin-Planck statement leads to the violation of the Clausius statement, and *vice-versa*. This can be understand by following examples;

Example 1: Consider a refrigerator, shown on the left side of figure 10 (a), that requires no work to transfer Q_L amount of heat from a sink to a heat reservoir and thus clearly violating the Clausius Statement of second law. Suppose that heat engine (on the right side) also operates between the same heat reservoir and sink in such a way that this engine takes Q_H amount of heat from the heat reservoir and reject Q_L amount of heat to the sink as it does an amount of work $W = Q_H - Q_L$. The engine, of course, does not violet any law, but the refrigerator and engine together constitute a self-contained machine that takes heat $(Q_H - Q_L)$ from the heat reservoir and converts all this heat into work without producing any change in the sink. Therefore, the refrigerator and engine together constitute a clear violation of Kelvin-Planck statement of second law.

(a)

(b)

Figure 10 The equivalence of the Kelvin-Planck & Clausius Statement

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Example 2: Consider an engine, shown on the left side of figure 10 (b), that rejects no heat to the sink and, this is against the Kelvin-Planck statement of second law. Suppose, that a refrigerator (on the right side) also operates between the same heat reservoir and sink and uses up all the work performed by the engine. The refrigerator violates no law, but the engine and refrigerator together constitute a self-contained machine that transfers heat Q_L from the sink to the heat reservoir without producing any change elsewhere. Therefore, the engine and refrigerator together constitute a violation of the Clausius statement of the second law.

Therefore, we arrive at the conclusion that both statement of the second law are equivalent.

Clausius Theorem: Reversible Part of Second Law

Consider the smooth closed curve on the p - V diagram shown in figure 13. Since no two adiabatic lines can intersect, a number of adiabatic lines may be drawn, dividing the cycle into a number of adjacent strips. A zig-zag closed path may now be drawn consisting of alternate adiabatic and isothermal portions.

Figure 13 pV diagram of a reversible smooth closed cycle and zig-zag closed path is made up of alternating reversible isothermal and adiabatic processes.

Since no heat is transferred in the any adiabatic process, then, the heat transferred during all the isothermal portions is equal to the heat transferred in the original cycle. Consider the two isothermal processes ab at the temperature T_1 , during which heat Q_1 is absorbed, and cd at the temperature T_2 , during which heat Q_2 is rejected. Since ab and cd are bounded by the same two adiabatic curves, $abcd$ is a Carnot cycle, and we may write as

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad (53)$$

Let us now assign a sign convention for Q 's, positive for heat absorbed by the system and negative for heat rejected from the system. We may then write the eq. (53) as

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

where Q_1 is a positive and Q_2 is negative quantity. Since the isothermal curves ef and gh are bounded by the same two adiabatic curves, $efgh$ is also a Carnot cycle, and

$$\frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0$$

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If a similar equations is written for each pair of isothermal curves bounded by the same two adiabatic curves and if all the equations are added, then the result obtained is

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \dots = 0$$

Since no heat is transferred during the adiabatic portions of the zig-zag cycle, thus

$$\sum_{i=1}^N \frac{Q_i}{T_i} = 0 \quad (54)$$

where the summation is taken over the entire zig-zag cycle consisting of Carnot cycles. Now if the cycle is divided into a large numbers of adiabatic curves close together. If we connect these adiabatic curves with small isothermal curves, then these isothermal processes become infinitesimal (very small). Therefore, we may write for any reversible cycle,

$$\oint_R \frac{\delta Q}{T} = 0 \quad (\text{reversible}) \quad (55)$$

The loop integral signifies that the integration takes place over the complete cycle and R says that equation is *true only for reversible cycle*. This result, known as **Clausius theorem** is one part of *the Clausius statement of the second law of thermodynamics*.

Clausius Inequality: Irreversible Part of Second Law

Let us consider an irreversible cycle and calculate its closed integral. Figure 14. shows a heat reservoir at T_1 supplying a small quantity of heat δQ_1 , to an auxiliary reversible engine R . The purpose of R is to provide reversible heat to the irreversible engine I . Engine R rejects a small amount of heat δQ at temperature T that is supplied to the irreversible engine I . Engine I does a small work W during an irreversible cycle, so the combined system of engine R and engine I also performs an irreversible cycle.

Figure 14 An auxiliary reversible engine R and irreversible engine I .

The net work of the combined system, according to first law, equals $\oint \delta Q_1$. But the net work cannot be positive, according to second law. Moreover if equals to zero, then it should be reversible engine, is contrary to the irreversibility of engine I . So, we conclude

$$\oint_R \delta Q_1 < 0 \quad (56)$$

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that is, engine I generates heat that flows out of the system.

We have for reversible engine R , in differential form

$$\frac{\delta Q_1}{T_1} = -\frac{\delta Q}{T}$$

Integrating around a cycle

$$-\oint_R \frac{\delta Q}{T} = \oint_R \frac{\delta Q_1}{T_1}$$

However, T_1 is the constant temperature of reservoir, so

$$-\oint_R \frac{\delta Q}{T} = \frac{1}{T_1} \oint_R \delta Q_1 \quad (57)$$

The heat δQ rejected from R is absorbed by I . Thus the sign must change for irreversible system, i.e.,

$$\oint_I \frac{\delta Q}{T} = \frac{1}{T_1} \oint_R \delta Q_1$$

or,

$$T_1 \oint_I \frac{\delta Q}{T} = \oint_R \delta Q_1 < 0$$

from eq. (56). Since $T_1 > 0$, the result is

$$\oint_I \frac{\delta Q}{T} < 0 \quad \text{(irreversible)} \quad (58)$$

The eq. (58) provides the second part of the second law and is known as *the inequality of Clausius*. It states that *for an internally reversible cycle, the closed integral of the ratio of the heat absorbed by a system to the temperature at which the heat is received is always less than zero.*

Compare eq. (55) and (58) and conclude that *the closed integral is less than zero for an irreversible cycle and equal to zero for a reversible cycle.* Combining the two equations produces *the Clausius statement of the second law of thermodynamics*;

$$\oint \frac{\delta Q}{T} \leq 0 \quad (59)$$

Entropy

Let an initial equilibrium state of any thermodynamic system be represented by the point i on any p - V diagram, shown in Figure 15, denote a final equilibrium state by the point f . It is possible to take the system from i to f along any number of different reversible paths, since i and f are equilibrium states. Suppose the system is taken from i to f along the reversible path R_1 and then back to i again another reversible path R_2 . The two paths form a reversible cycle and from Clausius theorem we may write

$$\oint_{R_1, R_2} \frac{\delta Q}{T} = 0$$

The above integral may be expressed as the sum of two integrals, one for the path R_1 and the other for the path R_2 . Then, we have

$$\int_{R_1} \int_i^f \frac{\delta Q}{T} + \int_{R_2} \int_f^i \frac{\delta Q}{T} = 0$$

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or,
$$\int_{R_1}^f \frac{\delta Q}{T} = - \int_{R_2}^i \frac{\delta Q}{T}$$

since R_2 is a reversible path,

$$- \int_{R_2}^i \frac{\delta Q}{T} = \int_{R_2}^f \frac{\delta Q}{T}$$

and finally,
$$\int_{R_1}^f \frac{\delta Q}{T} = \int_{R_2}^f \frac{\delta Q}{T} \quad (60)$$

Since, R_1 and R_2 were chosen at random and represent any two reversible paths, the above equation expresses the important fact that $\int_i^f (\delta Q/T)$ is independent of the reversible path connecting i and f . Therefore, it follows from equation (60) that there exists a function of the thermodynamic coordinates of a system whose value at the final state minus its value at the initial state equals the $\int_i^f (\delta Q/T)$. This state function was named the **entropy** by Rudolf Clausius and is denoted by S .

Figure 15 Two reversible paths joining two equilibrium states of a system.

If S_i is the entropy at the initial state and S_f the entropy at the final state, then we have a finite change of entropy $S_f - S_i$ from state i to state f , given by

$$S_f - S_i = \int_{R}^f \frac{\delta Q}{T} \quad (61)$$

where the path from i to state f is any reversible path R . Thus the entropy change of the system between i and f is independent of the path.

If the two equilibrium state i and f are infinitesimally near then the integral sign may be eliminated and $S_f - S_i$ becomes dS , an infinitesimal change of entropy of the system. Eq. (61), then

$$dS = \frac{\delta Q}{T} \quad \text{(reversible)} \quad (62)$$

where dS is an exact differential of an actual function S , such as dU .

The unit of entropy depends on the unit of heat employed and the absolute temperature. It is measured in *calories/°K* or *ergs/°K* or *Joules/°K*.