

The Second Law of Thermodynamics

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The first law of thermodynamics presents the relation between the two forms of energy heat and work and how do they convert to each other. However this law failed to explain qualitatively this conversion process or what is the maximum amount of heat can be converted into work. The answer for this question is presented by the second law of thermodynamics.

However before considering this in details two terms must be explained which the **heat engine** and the **heat pump**.

The Heat Engine

It is defined as follows “a device operating in a thermodynamic cycle between two heat reservoirs and produces work when supplied with heat”. Fig (8-1) shows a representation of a heat engine.

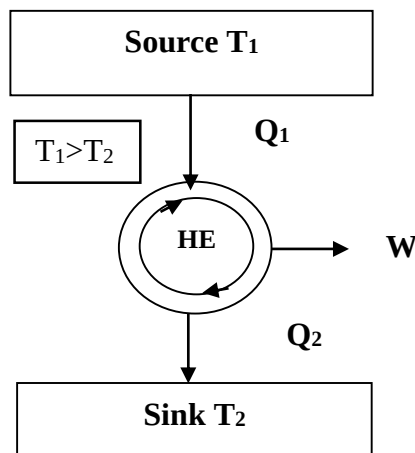


Fig (8-1) Schematic Representation of Heat Engine

This figure shows that the heat engine must operate between two heat reservoirs; a heat source and a heat sink. What is a heat reservoir? The heat reservoir is “the space whose temperature remains constant regardless of the quantity of heat added or heat removed”.

The temperature of the heat source is always higher than that of the heat sink. The heat engine converts part of the heat received from the heat reservoir into useful work and rejects the remaining to the heat sink. Apply the first law of thermodynamics.

$$\oint \delta Q = \oint \delta W$$

$$\therefore Q_1 - Q_2 = W \quad (8-1)$$

As mentioned earlier it is impossible to convert all heat into useful work. Therefore $Q_2 > 0$ always and $W < Q_1$. It is now possible to define a new term which is the **thermal efficiency** which is defined as follows “the ratio of net work done throughout the cycle or by the heat engine to amount of heat supplied”. It is given the symbol (η). The term efficiency is a general term for any process which is the ratio of output to input.

$$\therefore \eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad (8-2)$$

Since $Q_2 > 0$ the thermal efficiency is always less than 100% ($\eta < 100\%$).

There are a large number of practical engineering examples of heat engine we will consider few examples in the next sections.

The Steam Turbine Power Unit

This power unit produces electrical power from the heat generated by burning the hydrocarbon fuel extracted from crude oil. The unit consists of four main components which are; the boiler, the turbine, the condenser and the pump as shown in fig (8-2). The working fluid in this unit is water vapor (steam). It is clear from the fig that the working fluid flows in a cycle through these four components. The boiler represents the source where heat is supplied while the condenser represents sink where heat is rejected. The working fluid produces work as it expands in the turbine while work is done on the working fluid as it is pumped back to the boiler by the pump.

Apply the first law of thermodynamics on this plant,

$$\oint \delta Q = \oint \delta W$$

$$\therefore Q_1 - Q_2 = W_T - W_p \quad (8-3)$$

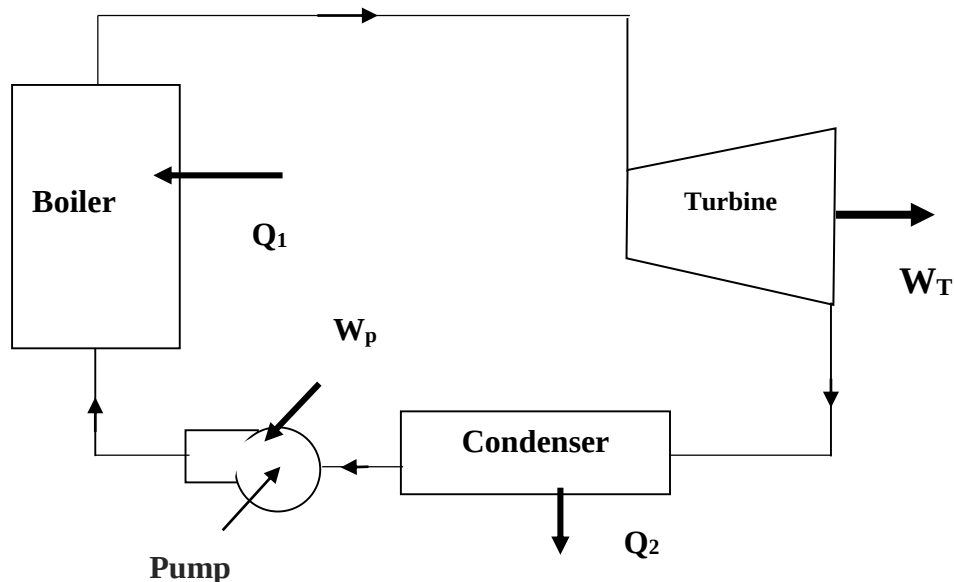


Fig (8-2) Schematic representation of Steam Turbine Power Unit

The Closed Cycle Gas Turbine Unit

The type of gas turbine unit consists of four main components which are, heater, turbine, cooler and compressor as shown in fig (8-3). The working fluid is air or any other inert gas. It flows in a closed cycle. It is heated in the heater, expanded in the turbine to generate work, cooled in the cooler and finally compressed by the compressor back to the heater pressure where work is done on the fluid in the compressor.

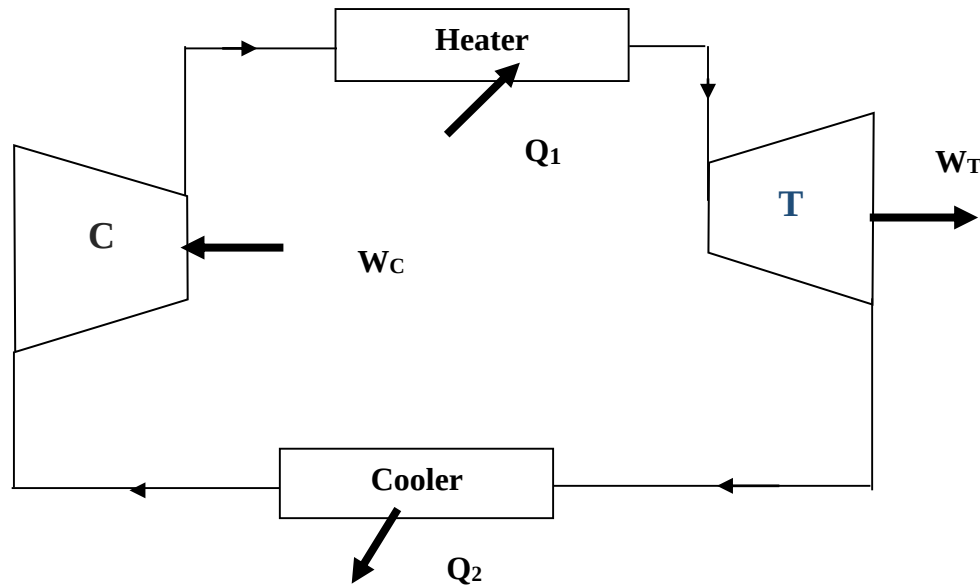


Fig (8-3) Schematic Representation Closed Cycle Gas Turbine Unit

Apply the first law of thermodynamics.

$$\oint \delta Q = \oint \delta W$$

$$\therefore Q_1 - Q_2 = W_T - W_C \quad (8-4)$$

The Open Cycle Gas Turbine Unit

This type gas turbine unit consists of three main components which are the combustion chamber, the turbine and the compressor in addition to the atmosphere to complete the cycle as in fig (8-4). In this system the chemical composition of the working fluid changes as it flows through the cycle. Air is drawn from the atmosphere, compressed in the compressor. The fuel is mixed with the air and burnt in the combustion chamber where heat (Q_1) is released and the combustion products expand in the turbine to generate work and finally expelled to the atmosphere where heat (Q_2) is rejected. This means the atmosphere is an essential part of the cycle. The combustion chamber represents the source where heat is liberated while the atmosphere represents the sink where heat is rejected.

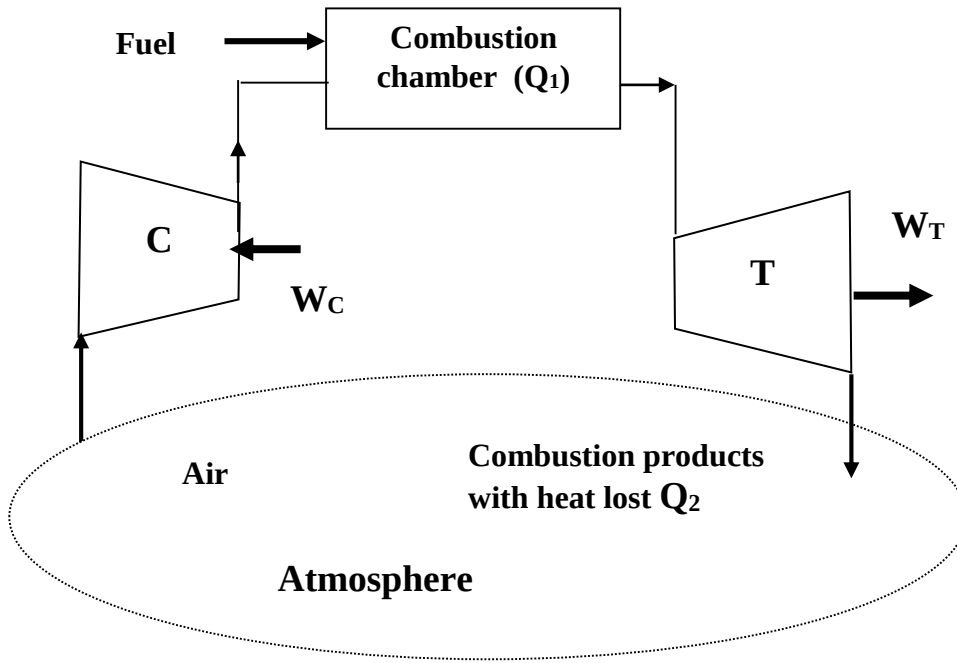


Fig (8-4) Schematic Representation of Open Cycle Gas Turbine

Apply the first law of thermodynamics,

$$\oint \delta Q = \oint \delta W$$

$$Q_1 - Q_2 = W_T - W_c$$

(8-5)

The Reciprocating Internal Combustion Engine

This engine consists of a single or a number of cylinders where a piston is reciprocating inside each cylinder. A combustible fuel air mixture is either inducted from outside or formed inside the cylinder. This mixture is ignited either directly or indirectly inside the cylinder and burnt to and combustion products expand inside the cylinder and do work on the piston. Finally the combustion products are expelled to the atmosphere with an amount of heat (Q_2). The system is shown schematically in fig (8-5). It is shown that the atmosphere is an integral components of the cycle from which air is withdrawn and to which combustion products are rejected.

Apply the first law of thermodynamics,

$$\oint \delta Q = \oint \delta W$$

$$\therefore Q_1 - Q_2 = W_{net}$$

(8-6)

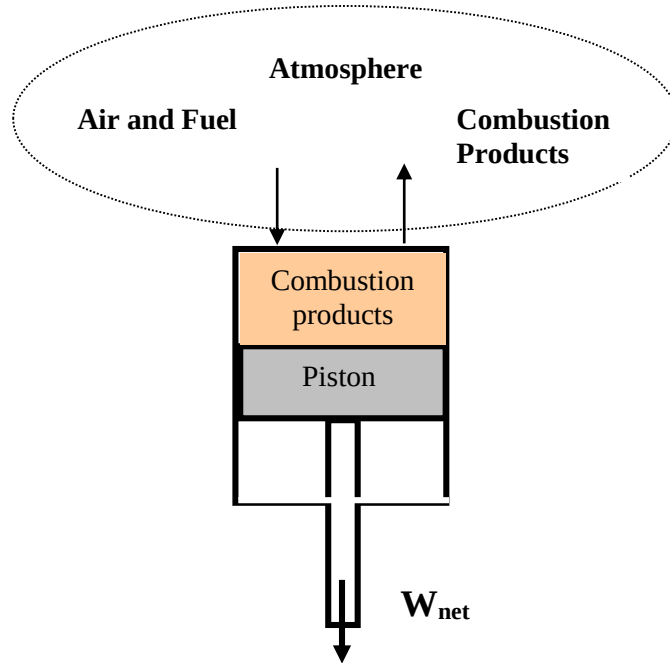


Fig (8-5) Schematic Representation of Reciprocating Internal Combustion Engine

The Heat Pump

The heat pump is defined as “a device operating in a cycle between two heat reservoirs and supplied with work to transfer heat from a cold space to a hot space”. Therefore we can say that the heat pump is the inverse of the heat engine as shown schematically in fig (8-6).

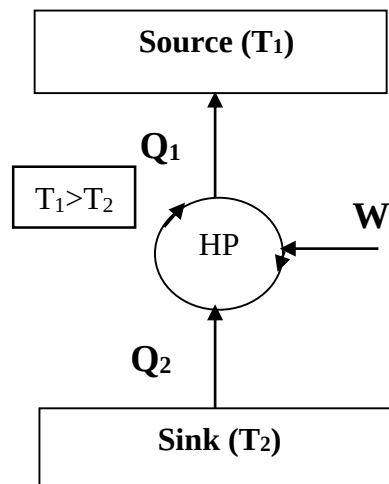


Fig (8-6) Schematic Representation of the Heat Pump

It is known that heat is transferred naturally from high temperature system to low temperature due to the temperature difference but to transfer heat from a low temperature system to a high temperature system work must be done. This is the function of the heat pump. It pumps the heat from the low temperature system to the high temperature system when work is consumed i.e. against the temperature gradient. This is the same as pumping a liquid from a low level to a high level by a pump.

If the heat pump is used to remove heat from a cold space it is referred to as the refrigerator while if it is used to add heat to an already hot space it is referred to as the heat pump.

Apply the first law of thermodynamics,

$$\oint \delta Q = \oint \delta W$$

$$-Q_1 + Q_2 = -W$$

$$\therefore Q_1 - Q_2 = W \quad (8-7)$$

When applying equation (8-7) the sign of heat and work must be taken into account as explained previously.

The term thermal efficiency is not used to describe the performance of a heat pump and another term is used which is the **COEFFICIENT OF PERFORMANCE (COP)**.

For the refrigerator the COP is “**the ratio between the heat removed from the cold space to the work consumed**”.

$$(COP)_c = \frac{\text{heat removed from cold space}}{\text{work required}}$$

$$(COP)_c = \frac{Q_2}{W} \quad (8-8)$$

The COP for the heat pump is “**the ratio between the heat added to the hot space to the work consumed**”.

$$(COP)_h = \frac{\text{heat added to hot space}}{\text{work required}}$$

$$(COP)_h = \frac{Q_1}{W} = \frac{W + Q_2}{W} = 1 + \frac{Q_2}{W} \quad (8-9)$$

$$\therefore (COP)_h = 1 + (COP)_c \quad (8-10)$$

Equation (8-9) indicates that the COP of the heat pump is the reciprocal of the thermal efficiency of the heat engine. The home refrigerator and the air condition systems are examples of the heat pump.

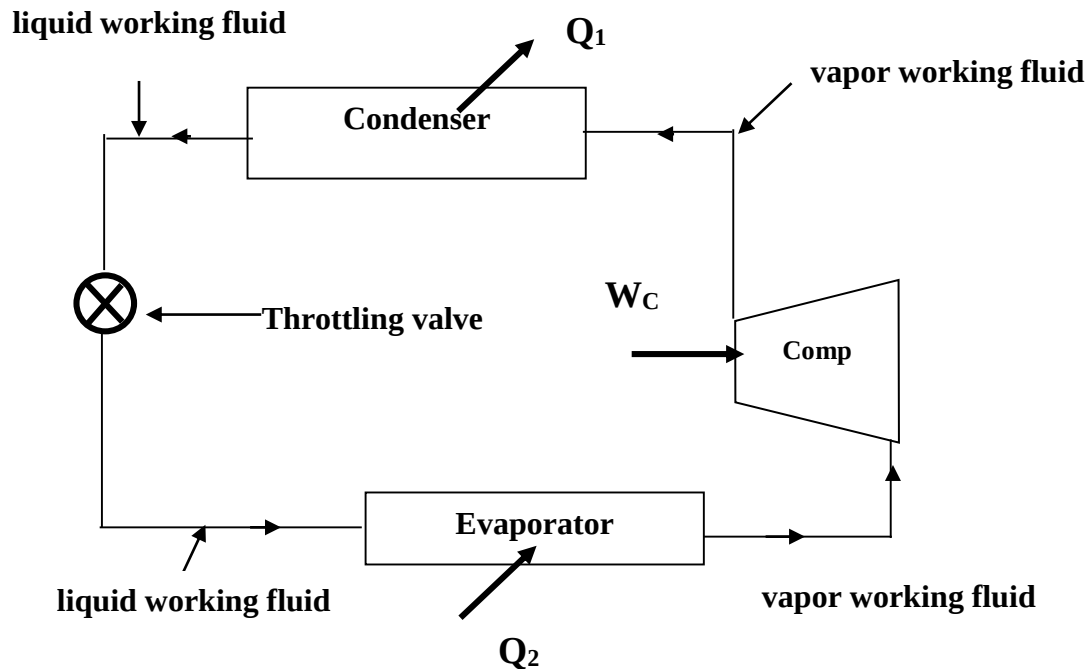


Fig (8-7) Schematic Representation of Refrigerator

Statements of the Second Law of Thermodynamics

There are many different statements for the second law of thermodynamics we will consider three only.

1-Carnot statement

This statement was proposed by the French scientist Sadi Carnot in 1824 as a result of his experimental work about converting heat into work in a heat engine. The statement is as follows **“the efficiency of the heat engine is independent of the type of working fluid but depends on the maximum and minimum temperatures within the cycle”**. According to equation (8-2) and this statement the thermal efficiency of the reversible heat engine is written as,

$$\eta = 1 - \frac{T_2}{T_1} \quad (8-11)$$

Where T_1 and T_2 are the temperatures of source and sink respectively.

The efficiency calculated from this equation is known as **Carnot cycle efficiency or Carnot engine efficiency**.

The engine that produces work without supply of heat is known as **“perpetual motion machine of the first kind”** since it violates the first law of thermodynamics and produces network larger than the net heat supplied.

2- Clausius statement

This statement was proposed by the German scientist Rodolf Clausius in 1850 depending on his experiments as follows **“It is impossible to design a device which operates in a cycle and produce no other effect other than heat transfer from a cold body to a hot body”**.

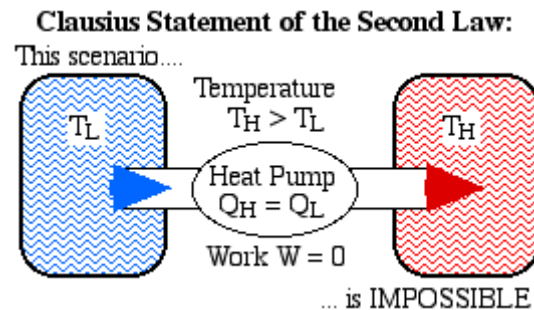


Fig (8-8)

3-Kelvin-Planck statement

Depending on previous experiments by Sadi Carnot Lord Kelvin concluded that if it is possible to produce work from a heat engine with no supply of heat it is possible to produce work from the cooling of a body only. However since both conclusions violate the first law of thermodynamics scientists Kelvin and Planck proposed the following statement for the second law of thermodynamics, **“It is impossible to construct a device which operates in a cycle and produces no other effect than the transfer of heat from a single reservoir in order to produce work”**.

The engine that produces work and exchanges heat with a single reservoir is known as the **“perpetual motion machine of the second kind”** since it violates the second law of thermodynamics.

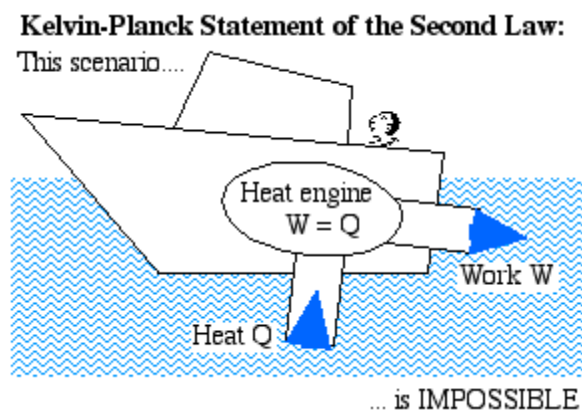


Fig (8-9)

These three statements are identical and the truth of each statement implies the truth of other statements. This can be proved as follows.

To prove the equivalence of the Kelvin and Clausius statements, we show that if one statement is false, it necessarily follows that the other statement is also false. Let us first assume that the Clausius statement is false, so that a refrigerator transfers all heat (Q) from a cold reservoir at a temperature (T_c) to a hot reservoir at a temperature (T_h) with no supply of work as shown in fig (8-10). Consider a heat engine operating between same temperatures (T_h and T_c) and extracts heat ($Q+\Delta Q$) from the hot reservoir, does work (W) and rejects heat (Q) to the cold reservoir as shown in same figure.

From the first law of thermodynamics.

$$W = (Q + \Delta Q) - Q = \Delta Q$$

Suppose these two devices are combined to form one device as shown in Figure.

The net heat removed from the hot reservoir is ΔQ and no net heat transfer occurs to or from the cold reservoir, and work W is done. Since $W = \Delta Q$ the combination forms a heat engine produces work (W) and exchanges heat with a single reservoir, thereby contradicting the Kelvin statement. Thus, if the Clausius statement is false, the Kelvin statement must also be false.

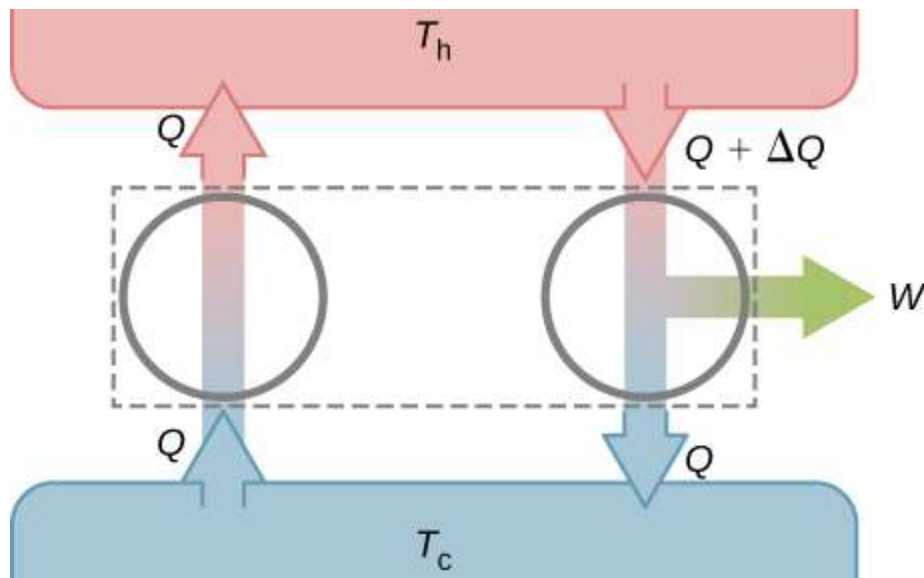


Fig (8-10)

Example 8-1

A heat pump is used in winter to heat a certain space so that the space temperature is 20 °C always. The rate of heat loss from the space is 25 kW when the outside temperature is -10 °C. Calculate the power required to drive this heat pump.

Since the heat pump is used as a heating device and the space is source and the outside environment is the sink.

$$\therefore (COP)_h = \frac{Q_1}{W}$$

The COP is the inverse of the thermal efficiency.

Assume that the thermal efficiency equals Carnot cycle efficiency.

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{263}{293} = 0.102 = 10.2\%$$

$$\therefore (COP)_h = \frac{1}{\eta} = \frac{1}{0.102} = 9.8$$

$$W = \frac{Q_1}{(COP)_h} = \frac{25}{9.8} = 2.55 \text{ kW}$$

Reversible and Irreversible Processes

According to Kelvin-Planck statement the heat engine must operate in a cycle between two heat reservoirs. This means that part of the heat supplied from the source is converted to useful while the other part must be rejected to the sink. Therefore the thermal efficiency of the heat engine must be always less than 100% according to equation (8-2). What is the maximum possible efficiency of a heat engine? The answer to this question becomes clear when the corollaries of the second law of thermodynamics are discussed in the next sections. First let us clarify the following two terms which are, the reversible process and the irreversible process.

The reversible process is defined as follows “the process during which the system and its surroundings can be restored to their initial states before the start of the process if we go back along the reverse path of the process”. There is another definition for the reversible process which is “the process whose path can be traced on the property diagram and can be represented by a mathematical relationship between fluid properties”.

The Irreversible process is defined as follows “the process during which neither the system nor the surrounding or both can be restored to the initial state before the start of the process. The path of the irreversible process cannot be traced on the property diagram and cannot be described by a mathematical any formula between fluid properties.

The presence of any of the following conditions during the process makes it irreversible.

1-Friction

2-Temperature difference between the system and its surroundings

3-Pressure difference between the system and its surroundings

4-Change of chemical composition of working fluid during the process.

Accordingly all real processes are irreversible since one or more of these conditions is always present during any real process.

Corollaries of the Second Law of Thermodynamics

These are complementary statements to the second law of thermodynamics as described below.

First Corollary

“It is impossible to construct a heat engine operating between two heat reservoirs that has a higher efficiency than a reversible heat engine operating between same two heat reservoirs”.

The reversible heat engine is the engine that operates in a thermodynamic cycle and all processes of this cycle are reversible. If one or more of the cycle processes is irreversible then the cycle becomes irreversible.

Assume,

η_R = efficiency of the reversible heat engine

η_{IR} = efficiency of the irreversible heat engine

The proof of this corollary depends on the assumption the irreversible heat engine has higher efficiency than the irreversible heat engine.

$$\eta_{IR} > \eta_R \quad (8-12)$$

Assume two heat engines one reversible and the other is irreversible operating between same two heat reservoirs as shown in fig (8-11). Each engine receives a quantity of heat Q_1 from the source. The work produced by the reversible heat engine is W_R and the work done by the irreversible heat engine is W_{IR} .

Since

$$\eta_{IR} > \eta_R$$

$$\therefore W_{IR} > W_R$$

Hence the heat rejected by the irreversible heat engine is less than that rejected by the reversible heat engine.

$$Q_1 - W_{IR} < Q_1 - W_R \quad (8-13)$$

Assume that the reversible heat engine is reversed to operate as a reversible heat pump. This heat pump transfers a quantity of heat $(Q_1 - W_R)$ from the sink to the source after doing work on the heat pump equals (W_R) . Therefore the total heat transferred to the source is (Q_1) .

Assume that the work W_R is supplied by the irreversible heat engine. This means that there is extra work equals $(W_{IR} - W_R)$ and no net heat exchange with the source. Therefore there is a device consists of the sink, the reversible heat pump and the irreversible heat engine operates in a cycle and produces work while exchanging heat with a single reservoir. This new device violates Kelvin- Planck statement.

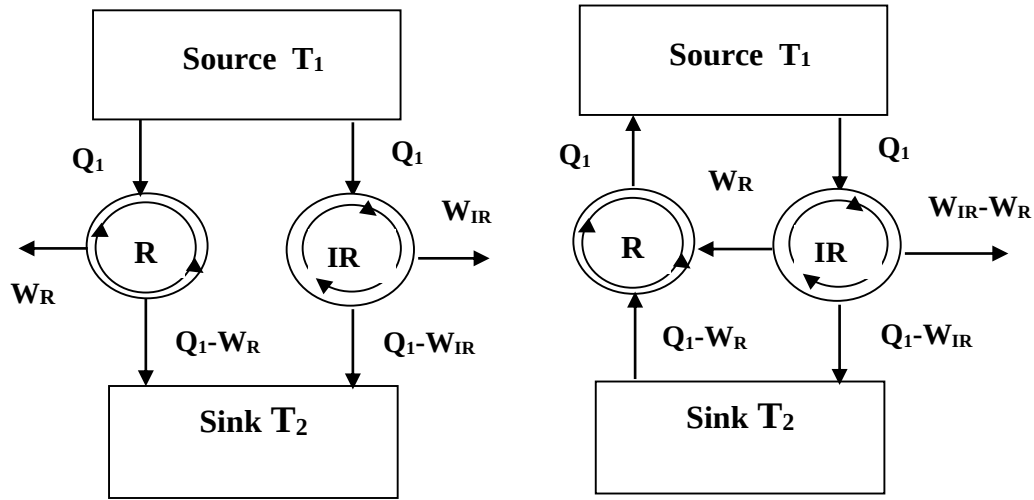


Fig (8-11)

This means that the initial assumption is incorrect since it generates a device violates the second law of thermodynamics.

Therefore the efficiency of the reversible heat engine must be higher than that of the irreversible heat engine.

$$\eta_R > \eta_{IR} \quad (8-14)$$

Second Corollary

It is stated as follows “**The efficiencies of all reversible heat engines operating between same two heat reservoirs are equal**”.

Assume two reversible heat engines R_1 and R_2 operating between same two heat reservoirs but have different efficiencies η_{R_1} and η_{R_2} .

Therefore, either $\eta_{R_1} > \eta_{R_2}$ or $\eta_{R_2} > \eta_{R_1}$

But according to the first corollary the reversible heat engine has the highest efficiency and since both engines are reversible and operating between same two heat reservoirs their efficiencies must be the highest hence they are equal.

$$\eta_{R_1} = \eta_{R_2} = \eta_C \quad (8-15)$$

According to this corollary it can be concluded that the efficiency of the reversible heat engine depends only on the temperatures of the heat reservoirs and independent of the type of working fluid.

$$\eta_c = 1 - \frac{T_2}{T_1} \quad (8-16)$$

η_c = Carnot cycle efficiency

T_1 = Source temperature

T_2 = Sink temperature.

Third Corollary

It is stated as follows “**A thermodynamic temperature scale can be defined that is independent of working medium and satisfies the absolute zero**”.

Assume a reversible heat engine operating between two reservoirs at temperature T_1 and T_2 . The efficiency of this engine is given as,

$$\eta = 1 - \frac{Q_2}{Q_1}$$

Since the engine is reversible its efficiency is equal to Carnot cycle efficiency and written as.

$$\eta = 1 - \frac{T_2}{T_1}$$

Comparing the above two equations yields that,

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} = f(T_1, T_2) \quad (8-17)$$

Consider a reversible heat engine (fig 8-12) operating between a source at temperature T_1 and different sinks at different temperatures. The engine is supplied by an amount of heat Q_1 from the source and heat rejected to each sink is measured. The measurement showed that there is a linear relationship between heat Q and temperature T as shown in fig (8-13).

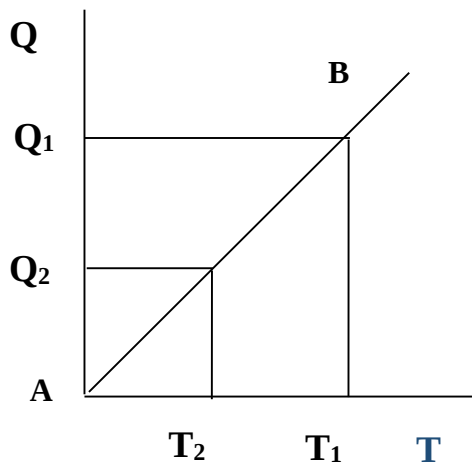


Fig (8-13) Relation between Q and T

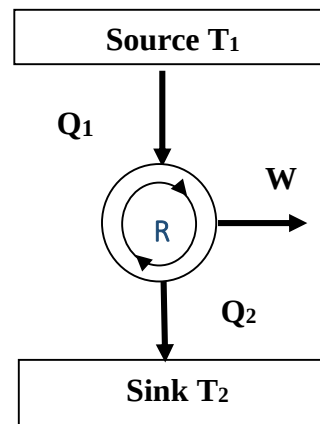


Fig (8-12) Reversible Heat Engine

The slope of the line AB in fig (8-13) equals the ratio $(\frac{Q}{T})$. Hence when,

$$Q=Q_1 \quad T=T_1 \quad \text{and when } Q=Q_2 \quad T=T_2$$

$$\text{Hence when } Q=0 \quad T=0.$$

The fraction $(\frac{1}{T})$ represents a unit of temperature through the range from $T=0$ to $T=T_2$ in a thermodynamic scale of temperature starting at absolute zero.

According to the second law of thermodynamics the heat rejected from any heat engine cannot be zero therefore the absolute zero cannot be attained. This can be explained as follows.

Assume a series of reversible heat engines each operating between two reservoirs and producing work (W) as shown in fig (8-14). The sink of the first engine acts as the source of the second engine and so on. Assume that the heat enters any reservoir equals the heat leaving this reservoir.

According to equation (8-17),

$$\frac{Q_o}{Q_1} = \frac{T_o}{T_1}, \quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}, \quad \frac{Q_2}{Q_3} = \frac{T_2}{T_3}, \quad \dots\dots\dots\text{etc}$$

The efficiency of each heat engine is,

$$\eta_1 = \frac{T_o - T_1}{T_o}, \quad \eta_2 = \frac{T_1 - T_2}{T_1}, \quad \eta_3 = \frac{T_2 - T_3}{T_2}, \quad \dots\dots\dots\text{etc}$$

$$\because \eta = \frac{W}{Q} \Rightarrow \therefore W = \eta Q$$

$$\because W_1 = W_2 = W_3 = \dots\dots\dots\text{etc}$$

$$\eta_1 Q_o = \eta_2 Q_1 = \eta_3 Q_2 = \dots\dots\dots\text{etc}$$

Substitute for the efficiency in the above equation,

$$\frac{T_o - T_1}{T_o} Q_o = \frac{T_1 - T_2}{T_1} Q_1 = \frac{T_2 - T_3}{T_2} Q_2 = \dots\dots\dots\text{etc}$$

$$\frac{Q_o}{T_o} (T_o - T_1) = \frac{Q_1}{T_1} (T_1 - T_2) = \frac{Q_2}{T_2} (T_2 - T_3) = \dots\dots\dots\text{etc} \quad (8-18)$$

The term $\frac{Q}{T}$ is the same for all engine as shown in fig (8-13) and can be omitted.

$$\therefore (T_o - T_1) = (T_1 - T_2) = (T_2 - T_3) = \dots\dots\dots\text{etc} \quad (8-19)$$

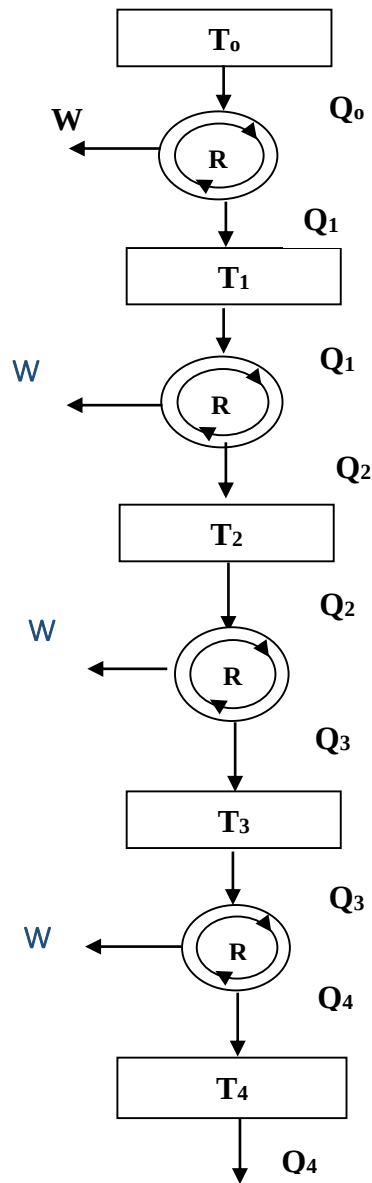


Fig (8-14) A series of Reversible Heat Engines

Equation (8-10) indicates that the temperature difference between successive reservoirs is constant and represents a degree on the suggested temperature scale. The maximum temperature in the series may be increased to any limit and minimum temperature in the series may be reduced to any limit by increasing the number of reversible engines. The last possible engine in the series is the engine that rejects heat to the next sink equals to the work done by this engine since the next engine converts all the heat into work and rejects no heat and this violates the second law of thermodynamics, hence it is impossible. This engine represents the absolute zero.

Fourth Corollary

It is stated as follows “**The efficiency of the reversible heat engine that operates between more than two reservoirs is less than its efficiency when operating between only two reservoirs whose temperatures are equal to highest and lowest temperatures of all reservoirs in the first case**”.

In the definition of heat reservoir it is mentioned that its temperature remains constant regardless of heat added or heat removed. This means that the temperature of the working fluid at which heat is supplied remains constant and the temperature of the working fluid at which heat is rejected remains also constant. However this not possible in real engines or real cycles since the temperature of the working fluid is always changing during heat supply and heat rejection. This does not mean that the engine becomes irreversible if each of the source and sink are assumed as a series of heat reservoirs with infinitesimal temperature difference.

If the temperature of source is T_1 and the temperature of the sink is T_2 then the efficiency of the reversible engine is,

$$\eta = 1 - \frac{T_2}{T_1} \quad (8-20)$$

Assume that T_1 and T_2 are the highest lowest temperature of the working fluid in the reversible engine which operates between more than two reservoirs. In this case part of the heat is supplied at temperature T_1 and part of the heat is rejected at temperature T_2 and the efficiency of converting this part only equals that calculated by equation (8-20). The rest of heat supplied is converted to with efficiency less than that calculated by equation (8-20) since it supplied at temperature less than T_1 and the rest of the rejected heat is rejected at temperature higher than T_2 . Therefore the efficiency of concerting all the heat supplied is less that the efficiency calculated by equation (8-20). This means that the efficiency of the reversible heat engine operating between more than two reservoirs is less than its efficiency when operating between two reservoirs whose temperatures are equal to the highest and lowest temperature of all reservoirs in the first case.

Fifth Corollary

This corollary is stated as follows “**When a system undergoes a thermodynamic cycle then the value of the term $\oint \frac{\delta Q}{T}$ equals zero if the cycle is reversible and less than zero if the cycle is irreversible**”. The mathematical formulation of this corollary is,

$$\oint \frac{\delta Q}{T} \leq 0 \quad (8-21)$$

This corollary is also known as **Clausius Inequality**.

First let us prove this corollary for the heat engine.

Assume the heat engine shown in fig (8-15).

According to the first law of thermodynamics,

$$\oint \delta Q = \oint \delta W = W_R$$

Since T_1 and T_2 are constant and according to the third corollary we conclude that,

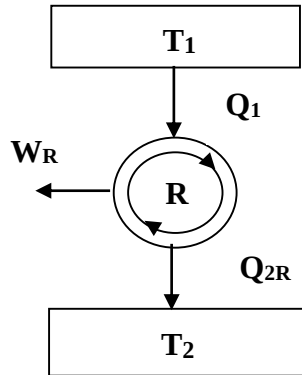


Fig (8-15) Reversible Heat Engine

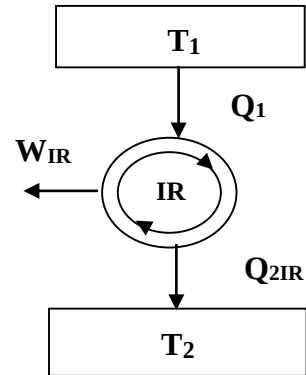


Fig (8-16) Irreversible Heat Engine

$$\frac{Q_1}{Q_{2R}} = \frac{T_1}{T_2} \quad ,$$

$$\frac{Q_1}{T_1} = \frac{Q_{2R}}{T_2}$$

$$\frac{Q_1}{T_1} - \frac{Q_{2R}}{T_2} = 0 \quad ,$$

$$\frac{Q_{2R}}{T_2} - \frac{Q_1}{T_1} = 0$$

$$\therefore \oint \frac{\delta Q}{T} = \frac{Q_1}{T_1} - \frac{Q_{2R}}{T_2} = 0 \quad (8-22)$$

As the value of T_1 approaches the value of T_2 with the cycle remains reversible the value of the term $\oint \delta Q$ approaches zero while the value of the term $\oint \frac{\delta Q}{T}$ remains zero. Therefore we conclude that for the reversible heat engine,

$$\oint \delta Q \geq 0 \quad (8-23)$$

$$\oint \frac{\delta Q}{T} = 0 \quad (8-24)$$

Assume an irreversible heat engine operates between the same two heat reservoirs and receives heat Q_1 from the source as in the previous case as shown in fig (8-16).

According to the first law of thermodynamics,

$$\oint \delta Q = Q_1 - Q_{2IR} = W_{IR}$$

Since the engine is irreversible,

$$\therefore W_{IR} < W_R$$

$$\therefore Q_1 - Q_{2IR} < Q_1 - Q_{2R}$$

$$\therefore Q_{2IR} > Q_{2R}$$

According to the third corollary,

$$\oint \frac{\delta Q}{T} = \frac{Q_1}{T_1} - \frac{Q_{2IR}}{T_2} \quad (8-25)$$

By comparing equations (8-22) and (8-25) we conclude that,

$$\oint \frac{\delta Q}{T} = \frac{Q_1}{T_1} - \frac{Q_{2IR}}{T_2} < 0 \quad (8-26)$$

Also,

$$\oint \delta Q > 0 \quad (8-27)$$

As the engine becomes more irreversible with Q_1 , T_1 , T_2 remain constant the value of the term

$\oint \delta Q$ approaches zero and the value of the term $\oint \frac{\delta Q}{T}$ becomes more negative. Therefore we can

write for all irreversible heat engines,

$$\oint \delta Q \geq 0 \quad (8-28)$$

$$\oint \frac{\delta Q}{T} < 0 \quad (8-29)$$

Hence, from previous conclusions we can write that for all heat engine (reversible and irreversible),

$$\oint \delta Q \geq 0 \quad (8-30)$$

$$\oint \frac{\delta Q}{T} \leq 0 \quad (8-31)$$

By the same methodology Clausius inequality can be proved for the heat pump.

Assume the reversible heat pump shown in fig (8-17). According to the first law of thermodynamics,

$$\oint \delta Q = -Q_{1R} + Q_2 < 0 \quad (8-32)$$

$$\oint \frac{\delta Q}{T} = -\frac{Q_{1R}}{T_1} + \frac{Q_2}{T_2} \quad (8-33)$$

$$\text{Since, } \frac{Q_{1R}}{T_1} = \frac{Q_2}{T_2}$$

$$\therefore \oint \frac{\delta Q}{T} = -\frac{Q_{1R}}{T_1} + \frac{Q_2}{T_2} = 0 \quad (8-34)$$

As T_1 approaches T_2 the value of the term $\oint \delta Q$ approaches zero while the value of the term $\oint \frac{\delta Q}{T}$

remains zero. Therefore we can write that for all reversible heat pumps,

$$\oint \delta Q \leq 0 \quad (8-35)$$

$$\oint \frac{\delta Q}{T} = 0 \quad (8-36)$$

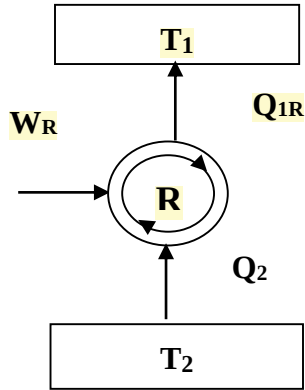


Fig (8-17) Reversible Heat Pump

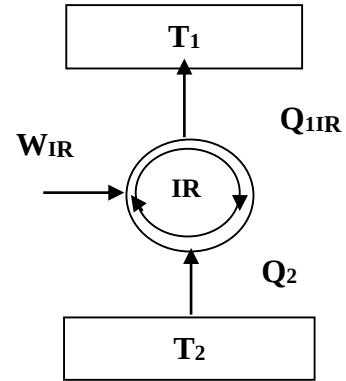


Fig (8-18) Irreversible Heat Pump

Assume an irreversible heat pump operating between same two heat reservoirs and transfers heat Q_2 from the sink as in the first case as shown in fig (8-18).

$$\therefore W_{IR} > W_R$$

This means that,

$$Q_{1IR} - Q_2 > Q_{1R} - Q_2$$

$$\therefore Q_{1IR} > Q_{1R} \quad (8-37)$$

According to the first law of thermodynamics,

$$\oint \delta Q = -Q_{1IR} + Q_2 \quad (8-38)$$

Since,

$$Q_{1IR} > Q_2 \quad (8-39)$$

$$\therefore \oint \delta Q < 0 \quad (8-40)$$

As T_1 approaches T_2 the value of the term $\oint \delta Q$ approaches zero.

$$\therefore \oint \delta Q \leq 0 \quad (8-41)$$

According to the third corollary,

$$\oint \frac{\delta Q}{T} = -\frac{Q_{1IR}}{T_1} + \frac{Q_2}{T_2} \quad (8-42)$$

From the comparison of equations (8-42) and (8-34) and according to equation (8-39) we conclude that,

$$\oint \frac{\delta Q}{T} = -\frac{Q_{1IR}}{T_1} + \frac{Q_2}{T_2} < 0 \quad (8-43)$$

Therefore we can generalize that for all heat pumps (reversible and Irreversible),

$$\oint \delta Q \leq 0 \quad (8-44)$$

$$\oint \frac{\delta Q}{T} \leq 0 \quad (8-45)$$

Therefore Clausius inequality is valid for all systems (reversible and irreversible)

$$\oint \frac{\delta Q}{T} \leq 0$$

Sixth Corollary

This corollary is stated as follows “when a closed system undergoes a reversible process between two states then there is a change in a property of the system equals $\int_1^2 \frac{\delta Q}{T}$ and this property is known as the “entropy”.

Assume a closed system undergoes a reversible process from state (1) to State (2) along path (A) and completes a thermodynamic reversible cycle by returning to its original state through a reversible process from state (2) to state (1) along path (B). The cycle is (1-2-1)_{AB} as shown in fig (8-19).

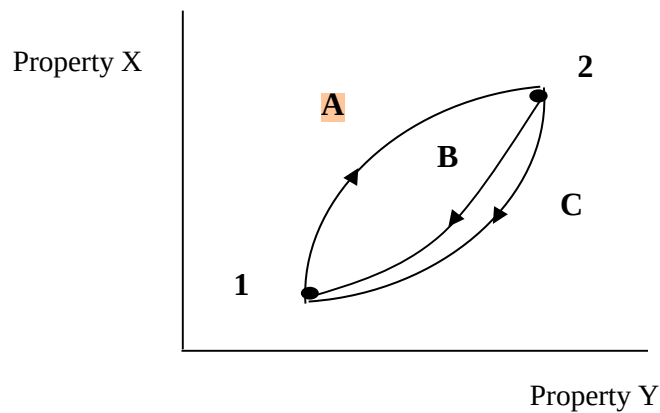


Fig (8-19) A property diagram to prove the sixth corollary

According to the fifth corollary and for a reversible cycle,

$$\oint \frac{\delta Q}{T} = 0$$

$$\therefore \int_1^2 \left(\frac{\delta Q}{T} \right)_A + \int_2^1 \left(\frac{\delta Q}{T} \right)_B = 0 \quad (8-46)$$

Assume that the same system completes a new cycle by returning from state (2) to state (1) through a reversible process along path (C) instead of path (B). The new cycle is (1-2-1)_{AC} is also reversible.

Again according to the fifth corollary and for a reversible cycle,

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T} \right)_A + \int_2^1 \left(\frac{\delta Q}{T} \right)_C = 0 \quad (8-47)$$

$$\begin{aligned} \therefore \int_1^2 \left(\frac{\delta Q}{T} \right)_A + \int_2^1 \left(\frac{\delta Q}{T} \right)_B &= \int_1^2 \left(\frac{\delta Q}{T} \right)_A + \int_2^1 \left(\frac{\delta Q}{T} \right)_C \\ \therefore \int_2^1 \left(\frac{\delta Q}{T} \right)_B &= \int_2^1 \left(\frac{\delta Q}{T} \right)_C \end{aligned} \quad (8-48)$$

Equation (8-48) indicates that value of the term $\int \frac{\delta Q}{T}$ is independent of the path of the process but depends on the end states of the process. Therefore this term represents the change in a property of the system. Hence the term $\left(\frac{Q}{T} \right)$ is a property of the system when it undergoes a reversible process. This property is known as the “entropy” and referred to by the symbol (S). Therefore,

$$dS = \left(\frac{\delta Q}{T} \right)_{rev} \quad (8-49)$$

This property is an extensive property since it depends on the mass of the system. The change in this property is given by the following equation,

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{rev} \quad (8-50)$$

The change of entropy per unit mass which is the specific entropy is given as,

$$s_2 - s_1 = \int_1^2 \left(\frac{\delta q}{T} \right)_{rev} \quad (8-51)$$

Seventh Corollary

This corollary is stated as follows “**when a thermally insulated closed system undergoes a reversible process its entropy remains constant but when the process is irreversible its entropy increases**”.

Since the system is thermally insulated then process is adiabatic ($\delta Q = 0$) and since the process is reversible and according to the sixth corollary,

$$s_2 - s_1 = \int_1^2 \left(\frac{\delta q}{T} \right)_{rev}$$

$$\therefore \delta q = 0$$

$$\therefore s_2 - s_1 = 0$$

$$\therefore s_2 = s_1 \quad (8-52)$$

This means that the entropy of the system during the reversible adiabatic process remains constant. Therefore this process is known as “**isentropic process**”.

The second part of this corollary is proved as below.

Assume a certain system undergoes an irreversible adiabatic process along path (A) as shown in fig (8-20).

$$\because \delta q = 0$$

$$\therefore \int_1^2 \left(\frac{\delta q}{T} \right)_A = 0$$

Assume that the system completes a cycle by a reversible process along path (B) which could be adiabatic or non-adiabatic.

$$\therefore \int_2^1 \left(\frac{\delta q}{T} \right)_B = s_1 - s_2$$

Since the process along path (A) is irreversible then the cycle (1-2-1)_{AB} is irreversible.

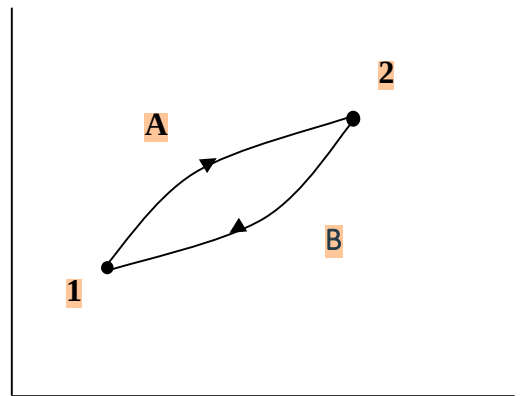
Hence according to the fifth corollary (Clausius inequality),

$$\oint \left(\frac{\delta q}{T} \right)_{AB} = \int_1^2 \left(\frac{\delta q}{T} \right)_A + \int_2^1 \left(\frac{\delta q}{T} \right)_B < 0$$

$$\because \int_1^2 \left(\frac{\delta q}{T} \right)_A = 0$$

$$\therefore \int_2^1 \left(\frac{\delta Q}{T} \right)_B < 0$$

Property Y



Property X

Fig (8-20) Schematic representation to prove the Seventh Corollary

However,

$$\int_2^1 \left(\frac{\delta q}{T} \right)_B = s_1 - s_2$$

$$\therefore s_1 - s_2 < 0$$

$$\therefore s_2 > s_1$$

(8-53)

Equation (8-53) indicates that when a system undergoes an irreversible adiabatic process its entropy will increase.

This corollary can also be proved for the open system as follows.

The sixth corollary indicates that the entropy is a property of the system since it depends on the end states of the process and independent of the path of the process or type of system whether closed or open.

Assume an adiabatic control volume with mass (m) and total entropy (S).

Assume a thermally insulated open system with steady flow. Since the flow is steady the properties of the control volume (including the entropy) will remain constant and independent of time. Assume that the steady flow process is a series of instantaneous non-flow processes where a mass (δm) with a specific entropy (s_1) enters the system and a mass (δm) with a specific entropy (s_2) leaves the control volume during each process. Hence the total entropy of the open system at the start of the process will be ($S + \delta m s_1$) and the total entropy of the system at the end of the process will be ($S + \delta m s_2$).

Since the entropy of the adiabatic closed system either increases or remains constant, hence,

$$\therefore S + \delta m s_2 \geq S + \delta m s_1$$

$$\delta m s_2 \geq \delta m s_1$$

$$\therefore S + \delta m s_2 \geq S + \delta m s_1 \quad (8-54)$$

$$\delta m s_2 \geq \delta m s_1 \quad (8-55)$$

Therefore for the thermally insulated steady flow system,

$$\sum \delta m s_2 \geq \sum \delta m s_1 \quad (8-55)$$

$$\therefore s_2 \geq s_1 \quad (8-56)$$

Equation (8-56) indicated that the specific entropy of steady flow processes is either increases or remains constant. For the reversible process the specific entropy remains constant ($s_2 = s_1$) while for the irreversible process the specific entropy increases ($s_2 > s_1$).

Third Law of Thermodynamics and the Absolute Entropy

The statement of the third law of thermodynamics was developed by the scientists W.H. Nernst and Max Planck at the start of the twentieth century. This statement is as follows

“The entropy of a pure, perfect crystalline substance at absolute zero is zero”. The pure crystal has a complete crystalline structure and therefore has the minimum internal energy. Substances with incomplete crystalline structure has a certain value of randomness or disorder therefore its entropy at absolute zero is greater than zero.

There is another statement for the third law of thermodynamics which is “Each substance has a certain value of entropy but it equals zero at absolute zero for complete crystalline structure substances”.

The third of thermodynamics provides a reference level to calculate the absolute entropy which is the entropy at a pressure of 0.1 MPa and temperature (T).

The change of entropy for any substance between the reference state and any other state can be calculated using the following equation with help of appendix.

$$s_{T,P} = s_T^o - R_o \ln\left(\frac{P}{P^o}\right) + (s_{T,P} - s_{T,P}^*) \quad (8-57)$$

where,

$s_{T,P}$ = the absolute entropy at (P) and temperature (T).

s_T^o = the absolute pressure at pressure 0.1 MPa and temperature (T).

$R_o \ln\left(\frac{P}{P^o}\right)$ = change in absolute entropy due to change in pressure from 0.1 MPa to pressure (P).

$(s_{T,P} - s_{T,P}^*)$ = correction factor for actual behavior of substance obtained from generalized entropy correction chart shown in fig (8-21).

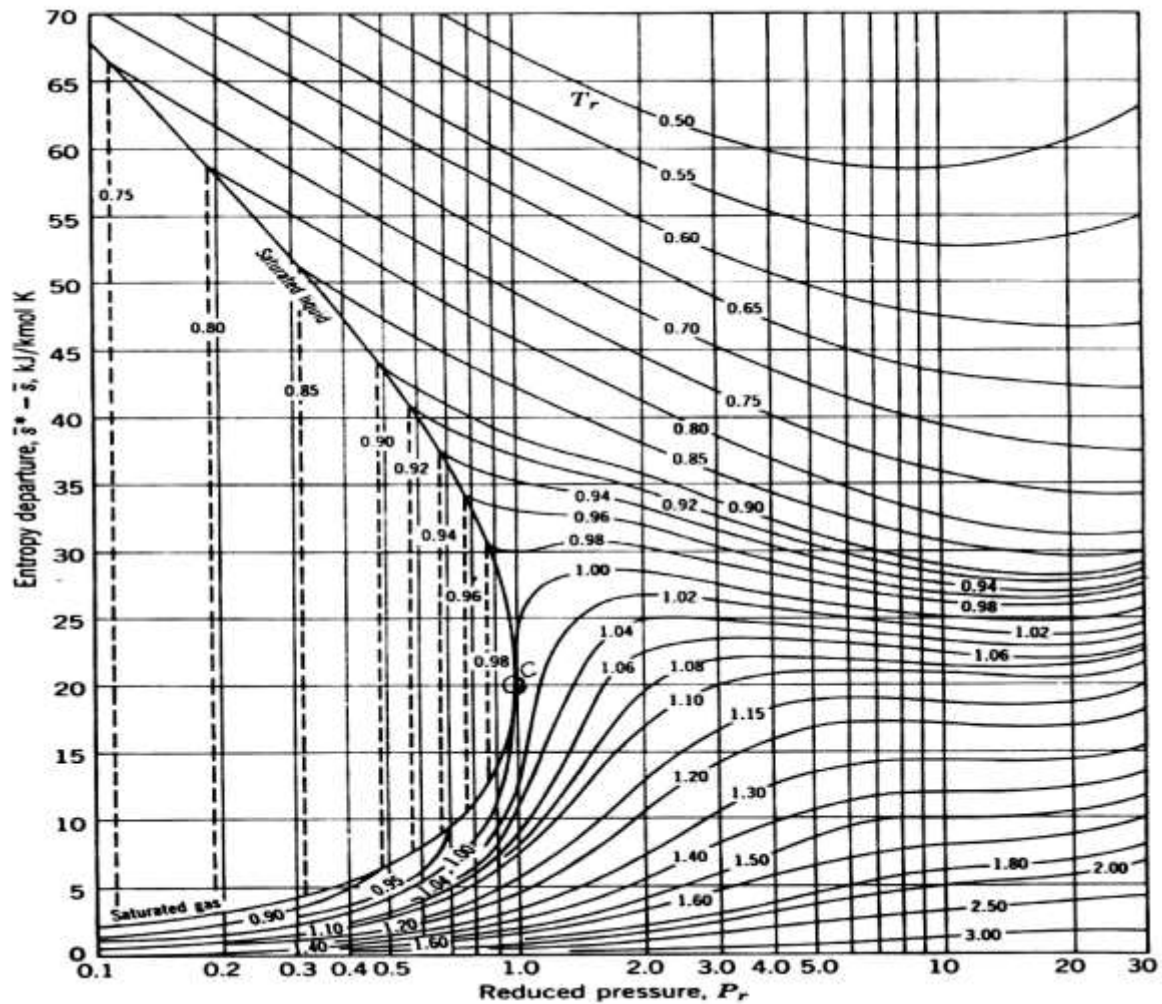


Fig (8-21) Generalized Entropy Correction Chart

From: Fundamentals of Classical Thermodynamics, third edition
Gordon J. Van Wylen and Richard E. Sonntag
John Wiley and Sons.