The Second Law of Thermodynamics

- **HEAT** is transferred spontaneously from a **hot object** to a **cold object**.

There are several equivalent ways to state the second law of thermodynamics. The above is just one of them ((later on we will mention other statements and show their equivalence.)

- A more general statement originated from the studies of **HEAT ENGINES**

  Cyclic conversion of **WORK** into **HEAT**: easy

  Cyclic conversion of **HEAT** into **WORK**: difficult

**HEAT ENGINE**: Device that changes thermal energy into mechanical work, performing such operation in a cyclic way.

The change in the internal energy of the heat-engine in a cycle is zero.
Example of Heat Engine

The Steam engine

Higher temperature

Intake valve (open during expansion)

Exhaust valve (closed during expansion)

Piston

Mechanical work

Notice:
A temperature difference is required to run the engine

Lower temperature
How team engines work

See animation of the engine in action at the website provided above.

Notice the need of both the high temperature (for the high pressure steam) and the low temperature (for the exhaust.)
Converting 100% of heat energy from an oven into work would be ideal, but that is not possible.

What governs then the maximum work that can be obtained from a heat engine?

What limits the maximum work one can obtain from a heat engine?

Why is a second heat reservoir needed to operate a heat engine?

1. The non-existence of perfect machines and the principle of increasing entropy

Conversion of work $w$ completely into heat

Fig. 1 Illustration of the conversion of mechanical work into heat.

Fig 2: Generalized schematic for showing the conversion of work $w$ into heat $q$ given off to a heat reservoir at temperature $T$.

Fig.1 and Fig.2 obtained from Reif, “Fundamentals of Statistical and Thermal Physics,” Mc. Graw-Hill, 1965

Here we define entropy $S$ as,
\[ S = \frac{q}{T} \] (q, heat transfer, T, temperature)

The process illustrated in Fig. 2 satisfies both:
- the first law.
  \[ \text{input energy in the form of work} = \text{output heat-energy to the reservoir} \]
- after the process the entropy of the whole universe has increased by \( \frac{q}{T} \).

**Perfect Heat Engine**
To what extent is it possible to proceed in the reverse way to figure 2?
That is, to what extend is it possible

1. to extract a net amount of energy from one reservoir (where that energy is randomly distributed over many degrees of freedom), and
2. to transform it into energy associated with the single degree of freedom connected with the external parameter of an outside device?

Figure 3 shows the prototype of the most desirable type of engine

![Perfect engine diagram](image)

The process illustrated in Fig. 3:
- satisfies the first law:
  \[ \text{input heat-energy from the reservoir} = \text{output energy in the form of work} \]
- after the process the entropy of the whole universe has been decreased by \( \frac{q}{T} \).

So the principle of increasing entropy, or at least remains the same, is violated by a perfect engine. In other words:

\[ \text{It is impossible to construct a perfect heat engine.} \]
\[ \text{(one that convert heat completely into work)} \]
This is known as the Kelvin’s formulation of the second law of thermodynamics.

**Real Heat Engine (the need of a second heat reservoir)**

What characteristic, then, has a real heat engine?
What do we need to fix in Fig. 3 so that the principle of increasing entropy is no violated?
How to make the total change in entropy (when converting heat into work) positive?

**Solution:**
What about if only part of the heat energy \(q\) (from the reservoir at temperature \(T\)) is converted into work \(w\), and the remaining amount of heat \((q-w)\) is given off to a reservoir of lower temperature \(T_{low}\).
If \(T_{low}\) is low enough, the increase in entropy \((q-w)/T_{low}\) may be high enough as to compensate or exceed \(q/T\).
Thus, while the universe loses entropy in the amount \(q/T\) (at the high temperature heat reservoir) it gains entropy by \((q-w)/T_{low}\). At the lower temperature heat reservoir
This will require that,

\[-q/T + (q-w)/T_{low} > 0\]  

\[q/T\]  
\[q-w\]  
\[T\]  
\[T_{low}\]  
\[w\]  
\[q\]  

For given temperatures \(T\) and \(T_{low}\), expression (2) places a **limitation on the maximum work possible to be attained from a heat machine**,  

\[w \leq q \left( 1 - \frac{T_{low}}{T} \right)\]  

(3)

If we define the efficiency \(\eta\) of a heat engine by,

\[\eta \equiv \text{work performed/ heat energy needed}\]

\[= w/q\]  

(4)

expression (4) indicated that the maximum efficiency of a heat engine is given by,
\[ \eta \leq \left( 1 - \frac{T_{\text{low}}}{T} \right) \]  

(5)

For given temperatures \( T \) and \( T_{\text{low}} \), the machine of optimum efficiency will be the one that has an efficiency equal to,

\[ \eta_{\text{max}} = \left( 1 - \frac{T_{\text{low}}}{T} \right) \]  

(6)

### 2. Carnot Engines

It is of interest, then, to show explicitly how such an engine of maximum efficiency \( \eta_{\text{max}} \), operating between two heat reservoirs, could be constructed.

It turns out, such an engine is the simplest conceivable engine and it is called a “Carnot engine” (named after Carnot, the French Engineer who was the first to examine theoretically the operation of heat engines).

Let \( x \) denote the external parameter of the engine \( M \); changes in this parameter give rise to the work performed by the engine. Let the engine initially be in the state where \( x = x_a \) and its temperature \( T = T_2 \) (the temperature of the colder heat reservoir).

The Carnot engine then goes through a cycle consisting of four steps, all performed in a quasi-static fashion. Label the macrostates of the engine by \( a, b, c, d \)

1. \( a \to b \): The engine is thermally insulated. Its external parameter is changed slowly until the engine temperature reaches \( T_1 \). Thus \( x_a \to x_b \) such that \( T_2 \to T_1 \).
2. \( b \to c \): The engine is now placed in thermal contact with the heat reservoir at temperature \( T_1 \). Its external parameter is changed further, the engine remaining at temperature \( T_1 \) and absorbing some heat \( q_1 \) from the reservoir. Thus \( x_b \to x_c \) such that heat \( q_1 \) is absorbed by the engine.
3. \( c \to d \): The engine is again thermally insulated. Its external parameter is changed in such a direction that its temperature goes back to \( T_2 \). Thus \( x_c \to x_d \) such that \( T_1 \to T_2 \).
4. \( d \to a \): The engine is now placed in thermal contact with the heat reservoir at temperature \( T_2 \). Its external parameter is then changed until it returns to its initial value \( x_a \), the engine remaining at temperature \( T_2 \) and rejecting some heat \( q_2 \) to this reservoir. Thus \( x_d \to x_a \) and heat \( q_2 \) is given off by the engine.

The engine is now back in its initial state and the cycle is completed.

Ideal Gas Carnot Engine
It is more common to see the analysis of Carnot cycles in which an ideal gas is used as the working substance.
The requirement that we must do the comparison at the beginning and at the end of the cycle is important.

Indeed, conversion of a given amount of heat-transfer $Q$ completely into macroscopic work $W$ can happen. That is observed, for example, during an isothermal expansion of an ideal gas (where $dU = 0$).

![Diagram of isothermal expansion](image)

In an isothermal expansion $\Delta U=0$, that is,

$$\Delta U = Q-W = 0 \quad \text{or} \quad Q=W$$

Accordingly, at the end of the expansion, a given amount of heat $Q$ will have been transferred to the gas, and its entirely will have been used by the gas to perform work. All the process happening at a single temperature $T$. However, this does not contradicts the Second Law because we have not left everything as it was before the isothermal expansion started; we have not completed the cycle.

(In passing, in the process 1 to 2, the entropy of the universe has not decreased: the heat reservoir loses entropy in the amount $\Delta Q/T$ and the system gains entropy due to the higher disorder in the wider volume. Hence $Q=W$ does not contradicts the physics law during a quasistatic isothermal expansion).
We could complete the cycle by allowing the gas to be compressed through the same isothermal (i.e., keeping constant the same temperature $T$ used during the expansion).

\[ W_{12} = W \]

\[ W_{21} = -W \]

The compression would restore the gas to its initial condition ($P = P_1$, $V = V_1$); that is, a cycle was completed. However, we realize that the net work done by the gas is zero \( (W_{12} + W_{21} = (W) + (-W) = 0) \). No useful work would have been obtained from the gas.

We know however that a net work can be obtained if we follow a cycle that uses two reservoirs at different temperatures.
Reversible Engines

Engines would work more efficient if there were not friction. When friction is present, part of the internal energy of the gas, that could be used to do useful work, ends up being converted to wasted heat.

An ideal (and very efficient engine) would be a frictionless engine (which we will consider in the following description).

In analogy with frictionless motion, we consider here a "frictionless" heat transfer:

Heat transfer whose direction we can reverse with only a tiny change of external parameters.
If the difference $T_1 - T_2$ is finite, it is not possible to make the heat flow in a reverse direction by a very small change in the temperature of either object.

But if one makes sure that heat flows always between two bodies at essentially the same temperature $T$, with just an infinitesimal difference ($+\Delta T$ or $-\Delta T$) to make it flow in the desired direction, the heat flow is said to be reversible.
The ideal engine is a reversible engine in which every process is reversible in the sense that, by infinitesimal changes we can make the engine go in the opposite direction.

A reversible process ensures that all the variables (p, v, T, ...) characterizing the system have at all times definite values.

1. **Non-Reversible Process**

2. **Free Expansion**

1. **Isothermal Expansion**

2. **Reversible Process**
Example of reversible cycle process

**Step 1** Isothermal expansion at $T_1$

\[ PV = nRT \]

As the gas expands, it does work against the external pressure $P$. $T_1$ Pad

Doing work would make the internal energy of the gas to decrease (i.e. its temperature would tend to decrease)

But, the pad at $T_1$ prevents the gas from decreasing its temperature by providing an amount of heat $Q_1$.

**Step 2** Adiabatic expansion

\[ PV' = \text{const} \]

The gas is allowed to expand, which causes the gas to do work.

Its internal energy decreases, and its temperature decreases to $T_2$. 

$T_1$ $T_1$ $T_1$
Step 3: Isothermal compression at $T_2$

Step 4: Adiabatic compression

Notice: The area within the 4 curves is equal to the net work $W$ done by the gas in one cycle.

The First Law implies:

$$\Delta Q_1 - \Delta Q_2 = W$$

*Net work done by the gas*
Conservation of energy $\Rightarrow\quad Q_1 = Q_2 + W$

Heat engine efficiency $\eta$:

$\eta = \frac{W}{Q_1}$, definition

Notice $\quad \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$,
A heat engine

High Temperature

Steam

Intake Valve (open during expansion)

Exhaust Valve (closed during expansion)

Piston

Mechanical Work

Low Temperature

Pump

Water

Condenser

Notice: A temperature difference is required to run the engine.
Suppose there were no condenser or pump, and that the steam was at the same temperature throughout the system. This would imply that:

The pressure of the gas being exhausted = the pressure of the gas at the intake

which means

work done by the gas on the piston would require an equal amount of work done by the piston on the gas to force it out the exhaust.

Hence

No net work would have been done.

In a real engine, the exhaust is cooled to a lower temperature so that the exhaust pressure is less than the intake pressure.

Thus, although the piston must do work on
the gas to expel it on the exhaust stroke, it is less than the work done by the gas on the piston during the intake.

\[ \text{work done on the piston by the gas} \]

\[ \text{work done by the piston on the gas} \]

So, a net amount of work is obtained but only if there is a difference of temperature.
Notice also, since this process is reversible, each step can be run backwards.

This process has the net effect of carrying heat from a cold reservoir ($T_2$) to a hot reservoir ($T_1$)!

It is a refrigerator.

The first law implies

$$Q_2 + W = Q_1$$

\[\text{External work done on the gas}\]
the value of $Q_1$ in (1) is the same that appears in (2). Similarly for the other quantities.
Example

An automobile engine has an efficiency of 20% and produces an average of 23,000 J of mechanical work per second during operation. How much heat is discharged from this engine per second?

Solution

\[ e = 1 - \frac{Q_L}{Q_H} \Rightarrow \frac{Q_L}{Q_H} = 0.8 \quad (1) \]

Also, \[ e = \frac{W}{Q_H} \Rightarrow Q_H = \frac{W}{e} = \frac{23,000 \text{ J}}{0.2} = 1.15 \times 10^5 \text{ J} \]

Replacing \( Q_H \) in (1) we obtain

\[ Q_L = 0.8 \quad Q_H = 0.8 \times 1.15 \times 10^5 \text{ J} = 0.92 \times 10^5 \text{ J} \]

The engine discharge 0.92 x 10^5 watts
From the expression

\[ e = 1 - \frac{Q_L}{Q_H} \]

notice that the efficiency of an engine will be greater if \( Q_L \) can be made small.

Experience indicates that it has not been possible to reduce \( Q_L \) to zero.

If it were possible to make \( Q_L = 0 \), it would imply that \( e = 100\% \).

That such a perfect engine (running continuously in a cycle) is \textbf{not} possible.

Is another way of expressing the second law of thermodynamics:

"No device is possible whose sole effect is to transform a given amount of heat completely into work"
1. No engine operating between two given temperatures is more efficient than a Carnot engine.

2. Construction of a thermodynamic absolute temperature $\theta$ scale.

1. No engine operating between two given temperatures is more efficient than a Carnot engine

In a previous section of these notes, when describing the capabilities of heat engines, we derived an expression for the maximum efficiency of a Carnot engine based on the principle that the entropy of the universe should not decrease. This time we describe an alternative demonstration that does not take into account that principle of the increasing entropy. Instead we take only the Kelvin or the Clausius statements as the second law of thermodynamics. From there we plan to obtain that the quantity $dq/T$ plays an important role in the description of thermodynamics.

Kelvin statement

There exists no thermodynamic transformation whose sole effect is to extract a quantity of heat from a given heat reservoir and to convert it entirely into work.

Clausius statement

There exists no thermodynamic transformation whose sole effect is to extract a quantity of heat from a colder reservoir and to deliver it to a hotter reservoir.
A key aspect in the demonstration is that the machine C is the one that is reversible (the machine C’ may or may not be reversible).

Let’s assume,

\[ \eta' > \eta \]  

(3)

If (3) were true, let’s take advantage of such a greater efficiency to pump some heat to the reservoir of higher temperature.
Work $W'$ from engine $C'$ supplied to the Carnot engine $C$ operated in reverse,
(and in such a way that it takes an amount of heat $Q_1' = Q_1''$ from the lower temperature reservoir)

$$Q_2' = W' = Q_1'$$

**Fig. 2** Heat engine $C'$ working in tandem with the Carnot engine operated in reverse.

By choice: $Q_1 = Q_1'$

From (2): $Q_2 = \frac{W'}{\eta}$  \hspace{1cm} (3)

Note: If engine-C had not been reversible, we wouldn’t have been able to use expression (3).

[A no well efficient engine that produces little work when operated as a heat engine can still be operated in reverse, but with just little amount of work the machine will not be able to deliver a large amount of heat to the higher temperature heat reservoir. For example, assume that the heat engine is so inefficient that only $W \sim 0$ is performed when operated as a heat engine (i.e. $Q_2 = Q_1 + W \sim Q_1$; $Q_2$ is wasted almost entirely into $Q_1$). Then, when operated in reverse we cannot claim that with little work $W \sim 0$ we can deliver $Q_1$ almost completely into the high temperature reservoir as $Q_2$; that would violate the principle of increasing entropy since the gain in entropy $Q_2/T_2 \sim Q_1/T_1$ at the higher temperature reservoir would be lower than the loss in entropy $Q_1/T_1$ at the higher temperature reservoir. We are bringing the argument of increasing entropy argument just to justify why expression (3) cannot be used when a non-Carnot engine is used, but, otherwise, we are not using that argument explicitly in our derivations].
Notice in Fig. 2, after the two processes are completed,

- the engines are back to their initial state, and
- the net effect is that the reservoir of higher energy gains a net heat in the amount,

$$Q_2 - Q_2' = \frac{W'}{\eta} - Q_2'$$

Using (1)

$$= \frac{\eta' Q_2'}{\eta} - Q_2'$$

$$= \left(\frac{\eta'}{\eta} - 1\right)Q_2'$$

(4)

If we assume that $\eta' > \eta$, expression (4) would imply that after each cycle the high temperature reservoir gets energy for free (while the rest of the universe remains in the same state). This is a violation of the energy conservation. Therefore the assumption that $\eta' > \eta$ must be incorrect.

That is, no engine is more efficient than the Carnot engine.

**Corollary**

All Carnot engines operating between two given temperatures have the same efficiency.

"We thus come to Carnot’s brilliant conclusion: that if an engine is reversible, it makes no difference how it is designed, because the (maximum) amount of work one will obtain if the engine absorbs a given amount of heat at temperature $T_2$ and delivers heat at some other temperature $T_1$ does not depend on the design of the engine. It is a property of the world, not a property of a particular engine!" Ref: Feynman Vol-1 Ch-44.
Since, for fixed temperatures $T_1$ and $T_2$, the efficiency $\eta_{12}$ is invariant, it implies that $Q_1$ and $Q_2$ vary in the same proportion.

Notice also that in the description above the concept of temperature is alluded just intuitively; The values of those temperatures could have been given by the readings from a mercury thermometer. The description just needed to discern whether one temperature was higher than the other. However, the new result expressed in (6) (indicating the invariance of the efficiency $\eta_{12}$ of a reversible heat-engine) furnishes to define an **absolute temperature scale $\theta$ based on the amount of heat transfers** occurring in a **reversible machine**. Since the ratio of the amount of heat-transferred involved is independent of the specific heat machine, then this thermodynamic absolute scale would be independent of the particular material the thermometer is made of (the reversible machine becoming the thermometer).

For example, in Fig. 4 one can assign temperature values $\theta_1$ and $\theta_2$ to two corresponding heat reservoirs 1 and 2 according to the following relationship,

$$\frac{Q_1}{Q_2} \equiv \frac{\theta_1}{\theta_2} \tag{7}$$

For an arbitrarily selected fixed quantity of heat $Q_1$ (transferred to reservoir-1) and a fixed (and arbitrarily defined) value of $\theta_1$, expression (7), together with (6), states:

$$\theta_2 \equiv \frac{\theta_1}{1 - \eta_{21}} = (\frac{\theta_1}{Q_1})Q_2 \tag{8}$$

The higher the heat-transfer $Q_2$ from a reservoir-2 the higher value of $\theta_2$ to be assigned to reservoir-2. We thus obtain a temperature scale that varies linearly with $Q_2$.

The ratio of two temperatures $\theta_1/\theta_2 = 1 - \eta_{12}$ will be invariant (according to Carnot, hence independent of the material the thermometer is made of.)
Fig. 4 Assigning temperatures $\theta_1$ and $\theta_2$ to a reversible heat engine working between two heat reservoirs where the ratio $Q_1/Q_2$ is known. For an an arbitrarily selected value of $\theta_1$ the temperature $\theta_2$ is determined; $\theta_2 = \theta_1 / (1 - \eta_{21}) = (\theta_1/Q_1) Q_2$.

Notice in passing that, once such a temperature scale $\theta$ is established, the definition (7) also implicitly defines a quantity $S$,

$$S \equiv \frac{Q_1}{\theta_1} = \frac{Q_2}{\theta_2}$$

that appears to be conserved during the operation of a reversible heat engine: at one reservoir $S$ decreases by $Q_2/\theta_2$ but the the other reservoir $S$ increases by $Q_1/\theta_1$; the interchange occurs in such a way that the total $S$ remains the same.

2. Procedure to build a scale of the thermodynamic absolute temperature $\theta$

Ref: Kerson Huang, 2nd edition, John Wiley

We arrange a series of Carnot engines, all performing the same amount of work $W$ (see Fig.5).

$$Q_{n+1} - Q_n = W$$

by choice

The absolute temperatures $\theta$ are assigned according to,

$$\frac{Q_n}{Q_{n+1}} \equiv \frac{\theta_n}{\theta_{n+1}}$$

by definition

Expression (10) implies,
\[
\frac{Q_n}{\theta_n} \equiv \frac{Q_{n+1}}{\theta_{n+1}} = S \quad \text{Quantity independent of } n \quad (10)
\]

\[Q_n + Q_{n+1} = W\]

\[Q_{n+1} = \theta_{n+1}, \quad Q_n = \theta_n\]

\[Q_{n+2} = \theta_{n+2}, \quad Q_{n+1} = \theta_{n+1}, \quad Q_n = \theta_n\]

\[\theta_1 = 1^\circ, \quad Q_1 = W. \quad \text{(arbitrary selection)} \quad (11)\]

which sets the value of \( S \) for the particular construction displayed in Fig. 5),

\[S = \frac{Q_1}{\theta_1} = \frac{W}{1^\circ} \quad (12)\]
From (10), $\theta_n = \frac{Q_n}{S}$ and $\theta_{n+1} = \frac{Q_{n+1}}{S}$, which gives,

$$\theta_{n+1} - \theta_n = \frac{Q_{n+1} - Q_n}{S}$$

Using (9),

$$\theta_{n+1} - \theta_n = \frac{W}{S}$$

(13)

In (12) $S$ was conveniently chosen as $W/1^\circ$; thus,

$$\theta_{n+1} - \theta_n = 1^\circ$$

(14)

Fig. 5 depicts then an absolute thermodynamic scale, of equally spaced temperature marks, the step being equal to $1^\circ$. 
Carnot engine:

Cases of positive and negative work

Below we prove:

\[
\begin{align*}
Q_2 &= W + Q_1 \\
\text{If } W > 0 &\quad \text{then } Q_1 > 0 \text{ and } Q_2 > 0 \\
\text{If } W < 0 \text{ and } Q_1 < 0 &\quad \text{then } Q_2 < 0
\end{align*}
\]
The system above absorbs heat in the amount $Q_2 + |Q_1|$ and converts it into work, which, as assumed above, is positive. (That work can be used, for example, to lift a block with a pulley.)

Let’s now damp that amount of work $Q_2 + |Q_1|$ into the reservoir-2 (using for example the Joule’s experiment to demonstrate the equivalence between work and heat).

The net result of these two steps is,

$$W = Q_2 + |Q_1|$$

The net result is the transference of an amount of heat $|Q_1|$ from the lower temperature reservoir to the higher temperature reservoir,
with no other effect. But this contradicts Clausius statement. The assumption that $Q_1 < 0$ must be incorrect then.

Therefore $Q_1 > 0$

Since $W > 0$ then $Q_2 = W + Q_1$ is also greater than zero.

If $W < 0$ and $Q_1 < 0$ then $Q_2 < 0$

Proof:

From (1),

$$Q_2 = W + Q_1$$

$$Q_2 = -|W| - |Q_1| < 0$$
Irreversibility and Entropy Changes
But we have changed the text substantially

Entropy change of the universe (system + reservoirs)

Reversible process

In general, reversible processes are accompanied by heat exchanges that occur at different temperatures.

![Fig. 1](image)

To analyze this process, one can visualize a sequence of heat reservoirs at different temperatures so that during any infinitesimal portion of the process the system is arbitrarily close to equilibrium.

During a differential change of states (at temperature $T$) the following occurs:

- Heat in the amount of $dQ_{\text{rev}}$ is absorbed by the system (a similar argument follows if the system reject an amount of heat). The entropy change of the system is

$$dS_{\text{system}} = \frac{dQ_{\text{rev}}}{T}. \quad (1)$$

- The entropy change of the reservoir is,

$$dS_{\text{reservoir}} = -\frac{dQ_{\text{rev}}}{T}. \quad (2)$$
The total entropy change of the system plus surroundings is

\[ dS_{\text{total}} = dS_{\text{system}} + dS_{\text{reservoir}} = 0 \]  \hspace{1cm} \text{(in a differential process)} \hspace{1cm} (3)

Since (3) is true for every differential path, then it is also true for the whole reversible process.

\[ \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{reservoir}} = 0 \]  \hspace{1cm} (4)

The conclusion is that for a reversible process, \( \text{A} \overset{\text{Reversible}}{\rightarrow} \text{B} \), the entropy of the system plus the entropy of the surroundings do not change:

\[ \Delta S_{\text{total}} = 0 \]  \hspace{1cm} (5)

**Entropy change of the system**

**Irreversible process.**

\[ \text{Comparison } \text{A} \overset{\text{Irreversible}}{\rightarrow} \text{B} \]

\[ \text{A} \overset{\text{Reversible}}{\rightarrow} \text{B} \]

Fig. 2 Irreversible and reversible paths connecting the states A and B.

Along the **irreversible path process** (Fig. 2), the system receives heat \( Q_{\text{irrev}} \) and does work \( W_{\text{irrev}} \). The net change between the states A and B is expressed as,

\[ U_B - U_A = Q_{\text{irrev}} - W_{\text{irrev}} \]  \hspace{1cm} \text{(First law)} \hspace{1cm} (6)

Along the reversible path process (Fig. 2),

\[ dU = TdS - dW_{\text{rev}} = 0 \]
\[ U_B - U_A = \int_A^B T \, dS - W_{\text{rev}} \]  

(7)

Because the state change is the same in the two processes, the change in internal energy is the same. Equating the changes in internal energy in the above two expressions yields

\[ Q_{\text{irrev}} - W_{\text{irrev}} = \int_A^B T \, dS - W_{\text{rev}} \]

\[ W_{\text{rev}} - W_{\text{irrev}} = \int_A^B T \, dS - Q_{\text{irrev}} \]

(8)

**Irreversible process. Differential path** \( A \longrightarrow A' \)

Comparison \( A \xrightarrow{\text{Irreversible}} A' \)

\[ A \xrightarrow{\text{Reversible}} A' \]

Alternatively, consider a irreversible process composed of infinitesimal quasi-static states. Within each quasi-static process we apply the differential version of the first law. So, we re-write (6) to (8) in differential form.

\[ dU = \delta Q_{\text{irrev}} - \delta W_{\text{irrev}} \]  

(First law)  

(9)

For the reversible process
\[ dU = T\, dS - \delta W_{\text{rev}} \]  

(10)

Because the state change is the same in the two processes, the change in internal energy is the same. Equating the changes in internal energy in the above two expressions yields

\[ \delta Q_{\text{irrev}} - \delta W_{\text{irrev}} = T\, dS - \delta W_{\text{rev}} \]

\[ \frac{1}{T} [\delta W_{\text{rev}} - \delta W_{\text{irrev}}] = dS - \frac{\delta Q_{\text{irrev}}}{T} \]  

(11)

Irreversible process.

Before proceeding, let’s address the Clausius inequality relating \([S_B - S_A]\) and \(\int_A^B \frac{\delta Q_{\text{irrev}}}{T}\)