

Chapter I :

Thermodynamics generalities

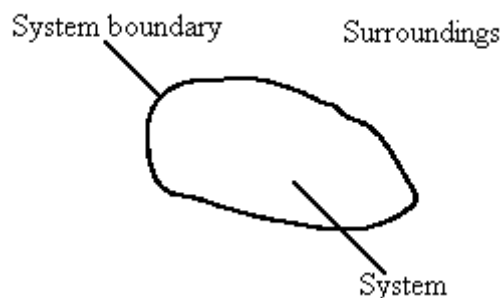
I- Introduction :

Thermodynamics is the science that deals with heat and work and these properties of substances that bear a relation to heat and work. Like all sciences, the basis of thermodynamics is experimental observation. In thermodynamics these findings have been formalized into certain basic laws, which are known as the first, second, and third law of thermodynamics. In addition to these laws, the zeroth law of thermodynamics, which in the logical development of thermodynamics precedes the first law.

II- Basic concepts in thermodynamics:

II-1- Thermodynamic system and external environment :

A thermodynamic system is defined as a quantity of matter of fixed mass and identity on which attention is focused for study. Everything external to the system is the surroundings, and the system is separated from the surroundings by the system boundaries. These boundaries may be either movable or fixed.



II-2- Types of thermodynamic systems :

We can distinguish the following cases

a- Isolated system: in an isolated system, there is no exchange between the system and the external environment, the system exchanges neither matter nor energy with its surroundings. As a result, the energy of an isolated system is conserved and can change form. In this case, the system undergoes a transformation.

b- Closed system: the system exchanges energy and heat with the external environment, but does not exchange matter.

c- Open system: all types of exchange are possible.

Recap table

System	Matter exchange	Energy exchange
Isolated	No	No
Closed	No	Yes
Opened	Yes	Yes



Examples :

- 1- A thermos flask is the best example of an isolated system. A thermos flask is used to keep things either cold or hot. Thus a thermos does not allow energy for transfer (**isolated system**).
- 2- Liquid water boiling in a saucepan (**open system**).
- 3- Example-When we boil water with a closed lid, the heat can exchange but matter cannot. (**closed system**).

II-3- Description of a thermodynamic system :

II-3-1-State of a thermodynamic system :

The state of the system is defined by macroscopic variables (m , P , T , V , etc.). A system is thermodynamically at equilibrium if its state variables have well -defined, constant values.

a- State variables

A system is characterized by state variables: volume 'V', pressure 'P', temperature 'T' and quantity of matter 'n'. The mathematical relationship between state variables is called the equation of state.

b- State function

A state function is a quantity such as 'P' whose value is known, while the state variables (n, V and T) are known. The relationship between P, V and T is given by the following equation:

$$f(P, V, T, n) = 0 ; \text{ called the equation of state.}$$

For a perfect gas: $P \cdot V - n R T = 0$ or ; $P V = n R T$

Variables	Functions
P ; V	$T = \frac{PV}{nR} \rightarrow f(P, V) = T$
V, T	$P = \frac{nRT}{V} \rightarrow f(V, T) = P$
P, T	$V = \frac{nRT}{P} \rightarrow f(P, T) = V$

II-3-2-Extensive and intensive quantities :

* **Extensive variables:** These are variables that depend on the quantity of matter and the size of the system. They are additive.

Ex: mass; length; surface area; volume; number of particles....

* **Intensive variables:** are non-additive variables that do not depend on the quantity of matter or the size of the system.

Ex: force; pressure; temperature; concentration....

II-4- Definition of certain thermodynamic variables :

II-4-1-Notion of pressure :

Pressure is the measure of force exerted per unit area of a system. It is a physical whose intensity is proportional to the number of impacts of atoms or molecules against the walls of a container.

The unit of pressure in (SI) is the pascal, abbreviation (Pa):

$$1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg/ms}^2$$

$$1 \text{ atm} = 1.01325 \cdot 10^5 \text{ Pa}$$

$$1\text{atm} = 1.01325 \text{ Bar}$$

$$1 \text{ atm} = 760 \text{ mmHg.}$$

II-4-2- Notion of temperature :

Temperature is a measure of how hot or cold an object or system is.

Temperature scales: centesimal, absolute and Fahrenheit

II-4-2-1- Centesimal

Its unit is the degree Celsius ($^{\circ}\text{C}$). This is a centesimal scale with two fixed points:

0°C , where ice melts, and 100°C , where water boils under standard pressure conditions.

II-4-2-2- Absolutes

Its unit is the kelvin (K), a scale linked to the centesimal scale by the relation:

At 273 K, the ice melts and 373 K water boils.

II-4-2-3-Fahrenheit

Its unit is the degree Fahrenheit ($^{\circ}\text{F}$). It is expressed by the relation:

At 32°F ice melts and at 212°F water boils.

Unit of 'T' (SI): K ; $T(\text{K}) = T(^{\circ}\text{C}) + 273$

II-4-3- Notion of volume :

Volume is defined as the three-dimensional space occupied by [matter](#) or enclosed by a surface.

The SI unit of volume is the cubic meter (m^3), but many units exist. Other volume units include the liter (L), cubic centimeter (cm^3)...

$$1 \text{ L} = 1\text{dm}^3; 1 \text{ ml} = 1\text{cm}^3; 1 \text{ L} = 10^{-3}\text{m}^3.$$

II-5- perfect gas :

A perfect gas consists of point-like particles with zero diameter and insignificant volume compared to their surroundings. This eliminates attraction and repulsion between gas molecules.

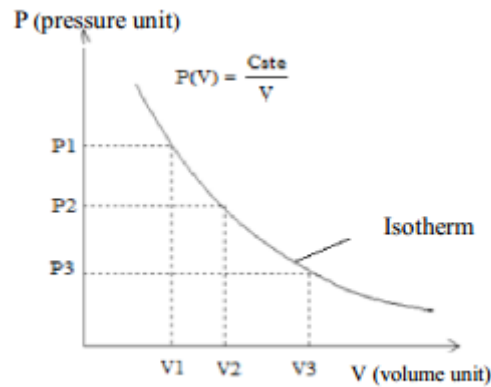
II-5-1- Perfect gas laws :

The perfect gas rigorously obeys the three laws. MARIOTTE, GAY LUSSAC and CHARLES.

II-5-1-1- MARIOTTE Law

Statement of the law: At constant temperature 'T', the product of the pressure 'P' of a gaseous mass and its volume 'V' is constant.: $P.V = Cte$

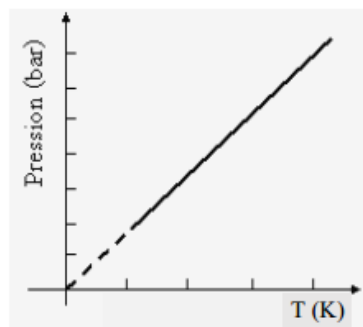
We have : $P.V = n.R.T$; $T = Cte \Rightarrow P.V = Cte \Rightarrow V \propto \frac{1}{P} \Rightarrow P = \frac{Cte}{V}$



II-5-1-2-GAY-LUSSAC law

It states that, at constant volume, the pressure of a quantity of gas is directly proportional to its temperature.

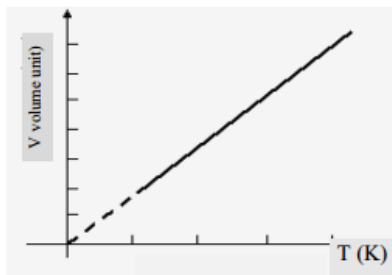
We have : $P.V = n.R.T$; $V = Cte \Rightarrow P = \frac{nR}{V}T = Cte .T \Rightarrow P \propto T$.



II-5-1-3-CHARLES law

It states that, at constant pressure, the volume occupied by a quantity of gas is directly proportional to its absolute temperature.

We have : $P.V = n.R.T$; $P = Cte \Rightarrow V = \frac{nR}{P}T = Cte .T \Rightarrow V \propto T$.



II-5-2-Avogadro's Law :

Avogadro's law, a statement that under the same conditions of temperature and pressure, equal volumes of different gases contain an equal number of molecules. Since equal numbers of molecules means equal number of moles, the number of moles of any gas is proportional to its volume, so $V \propto n$. The specific number of molecules in one gram-mole of a substance, defined as the molecular weight in grams, is $6.02214076 \times 10^{23}$, a quantity called Avogadro's number, or the Avogadro constant. For example, the molecular weight of oxygen is 32.00, so that one gram-mole of oxygen has a mass of 32.00 grams and contains $6.02214076 \times 10^{23}$ molecules.

The volume occupied by one gram-mole of gas is about 22.4 litres (0.791 cubic foot) at standard temperature and pressure (0°C , 1 atmosphere) and is the same for all gases, according to Avogadro's law.

II-5-3-Equation of state for perfect gas :

So far we have discussed three relationships of volume to which the perfect gas is subject

- MARIOTTE Law : $V \propto \frac{1}{P}$
- CHARLES law : $V \propto T$
- Afogadro Law : $V \propto n$

According to the laws of proportionality in mathematics :

$$\left. \begin{array}{l} V \propto \frac{1}{P} \\ \text{and} \\ V \propto T \end{array} \right\} \Rightarrow \left. \begin{array}{l} V \propto T \times \frac{1}{P} \\ \text{and} \\ V \propto n \end{array} \right\} \Rightarrow V \propto T \times \frac{1}{P} \times n \Rightarrow V = \frac{nRT}{P}$$

For a perfect gas: $P.V = n.R.T$

Where: P: gas pressure;

V: volume of the gas;

n: number of moles of the gas;

R: perfect gas constant;

T: gas temperature

- **Application**

Calculate the value of the perfect gas constant 'R'; for one mole of gas occupying a volume of 22.4L, under standard conditions (T= 0 °C and P = 1atm).

For : P = 1 atm ; V = 22.4 l ; n = 1 mol and T =273K , we have :

$$PV = nRT \Rightarrow R = \frac{PV}{nT}$$

$$P = 1\text{atm} = 1,01325 \cdot 10^5 \text{ Pa}; V = 22,4 \text{ l} = 22,4 \cdot 10^{-3} \text{ m}^3; T = 0 + 273,15 \text{ K};$$

$$n = 1 \text{ mole} \Rightarrow R = \frac{1,01325 \cdot 10^5 \times 22,4 \cdot 10^{-3}}{1 \times 273,15} \Rightarrow R = 8,314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\mathbf{R = 8.314 J/mol. K}$$

$$1\text{cal} = 4,18\text{J} \Rightarrow R = \frac{8,314}{4,18} = 1,987 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\mathbf{R = 2 cal/mol. K}$$

For : P = 1 atm ; V = 22.4 l ; n = 1 mol and T =273K , we have :

$$R = \frac{1 \times 22,4}{1 \times 273,15} = 0,082 \text{ l} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\mathbf{R = 0,082 atm.L/mol.K}$$

II-6-Dalton's law :

Dalton's law (also called **Dalton's law of partial pressures**) states that in a mixture of non-reacting gases, the total pressure exerted is equal to the sum of the partial pressures of the individual gases. This empirical law was observed by John Dalton in 1801 and published in 1802. Dalton's law is related to the ideal gas laws.

- **Formula**

Mathematically, the pressure of a mixture of non-reactive gases can be defined as the summation:

$$p_{\text{total}} = \sum_{i=1}^n p_i = p_1 + p_2 + p_3 + \dots + p_n$$

where p_1, p_2, \dots, p_n represent the partial pressures of each component.

$$p_i = p_{\text{total}} x_i$$

where x_i is the mole fraction of the i th component in the total mixture of n components

- **mole fraction**

In chemistry, the **mole fraction** or **molar fraction**, also called **mole proportion** or **molar proportion**, is a quantity defined as the ratio between the amount of a constituent substance, n_i (expressed in unit of moles, symbol mol), and the total amount of all constituents in a mixture, n_{tot} (also expressed in moles):

$$x_i = \frac{n_i}{n_{\text{tot}}}$$

It is denoted x_i (lowercase Roman letter x), sometimes χ_i (lowercase Greek letter chi). (For mixtures of gases, the letter y is recommended.)

III- Thermodynamic transformations :

III-1- change of state :

The thermodynamic process is a change of system from one state to another, such as raising the system's temperature (e.g. kettle). If the system is in a state of thermodynamic equilibrium, it can be changed by changing one or several of the state variables, such as temperature change, pressure change, volume, etc.

III-2-Closed and open transformations :

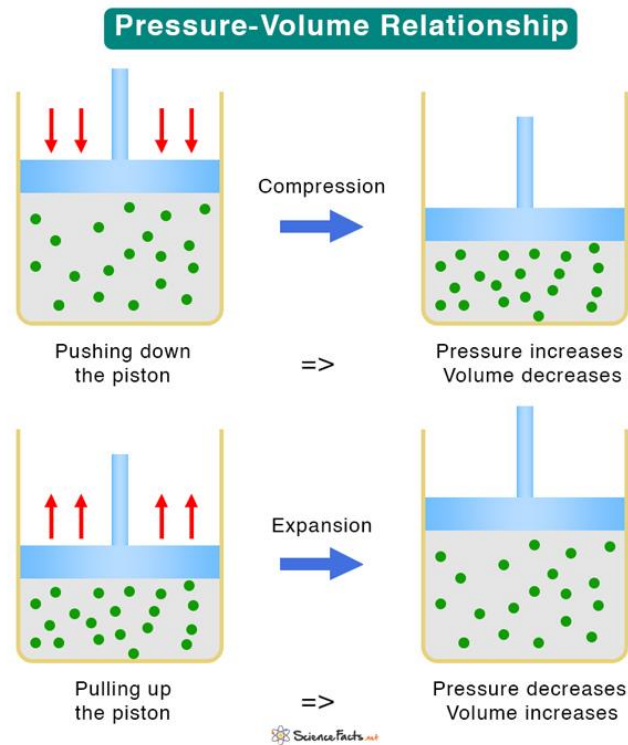
- **A cycle is a closed loop (closed transformations)** : the initial state is identical to the final state ($P_i ; V_i : T_i = P_f ; V_f : T_f$).
- **open transformations**: the initial state is different to the final state.

III-3- Representation of the thermodynamic transformations on the Clapyrone diagram :

A pressure-volume (PV) diagram is a graphical way of representing the relationship between the pressure and volume of an ideal gas. A PV diagram is drawn for a thermodynamic process occurring in a closed system, where there is no exchange of matter and energy between the system and its surroundings. The relationship between pressure and volume is causal, meaning a change in one results in a change in the other.

III-3- 1- Pressure and Volume Relationship :

To understand the pressure-volume relationship, consider a sealed container containing an ideal gas, as shown in the image below. It has a piston that, upon application of force, moves up and down to expand and compress the gas. The container, piston, and gas together comprise a thermodynamic system. If the piston moves down, the pressure increases, and the volume decreases. If the piston moves up, the pressure decreases, and the volume increases. Therefore, an increase in one quantity results in a decrease in the other.



Pressure and Volume Relationship

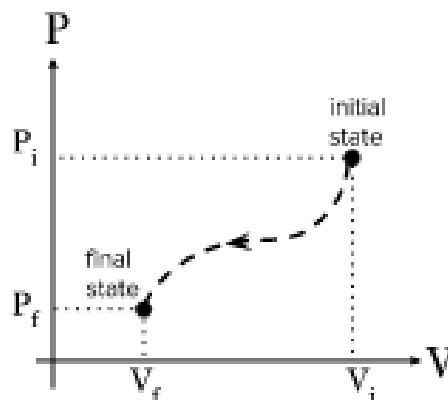
III-3- 2- How to plot a PV diagram :

Before we get into the details, let's look at how to plot a PV diagram (the following information will become more apparent as you read through this explanation!). To begin your plot, you will need to find the solutions and relationships between the **thermodynamic cycle**. Here is a helpful list of how to plot your PV diagrams:

1. **Identify the processes in the cycle.** How many processes does the gas go through? Which ones are they?
2. **Identify useful relationships between the variables.** Look for relationships such as "the gas doubles its pressure", "the gas decreases its temperature", or "the gas maintains its volume". This will give you helpful information on the direction of the

process in the PV diagram. An example of this is when the cycle or process increases its volume – this means the arrow goes from left to right.

3. **Look for keywords**, such as compression, expansion, no heat transfer, etc. These will tell you in which direction your process goes. An example is when you read “a gas compresses at constant temperature” – this is an isothermal line that goes from a lower pressure to a higher pressure (bottom to top).
4. **Calculate any variable that you need.** In the states where you don't have more information, you can use the gases laws to calculate variables you don't know. The remaining variables can give you more information about the process and its direction.
5. **Order your data and draw the cycle.** Once you've identified all your processes and have the information on each variable, order them by state. For example, state i (p_i, V_i, T_i), state f (p_f, V_f, T_f), and so on. Finally, draw the lines that link all states using the processes you identified in step 1.

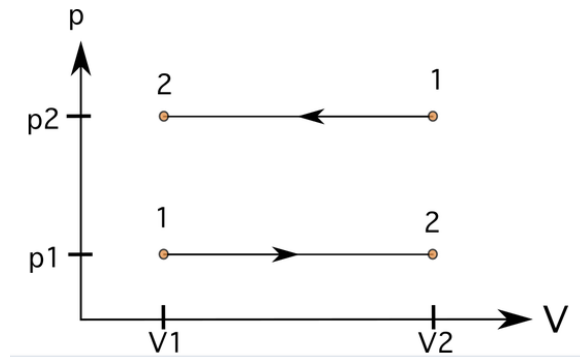


III-3- 3- Types of PV Diagrams :

We can associate four general thermodynamic processes with the container-piston system above.

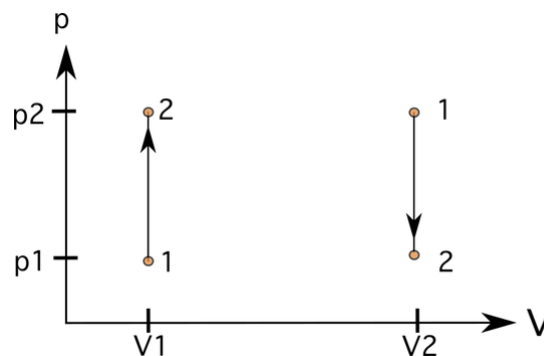
1. **Isobaric** – when the gas is held at a constant pressure ($P = Cte$):

In a constant pressure (isobaric) process, lines will be **straight, horizontal lines**. In these cases, the **area below the lines is regular**. you can see a process from state 1 to state 2 with increased volume (below) and a process going in the opposite direction from state 1 to state 2 (above).



2. Isochoric – when the gas is held at a constant volume ($V = Cte$):

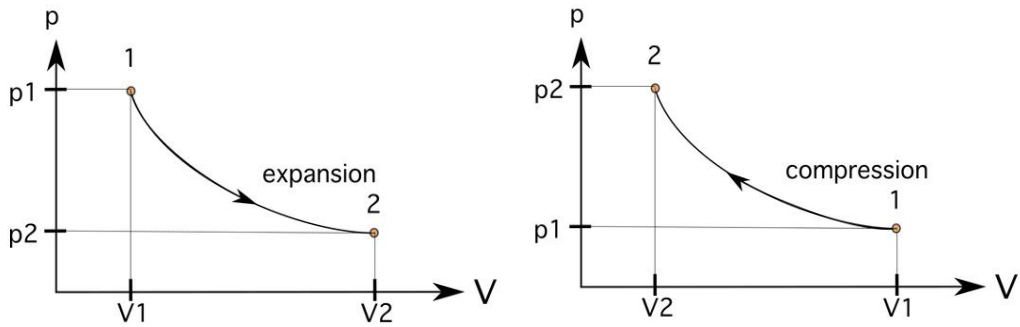
In a process with constant volume (isometric or isochoric), lines will be **straight, vertical lines**. There is **no area below the lines in these cases**. The diagram shows a process from state 1 to state 2 with increased pressure on the left and a process going in the opposite direction from state 1 to state 2 on the right.



3. Isothermal – when the gas is held at a constant temperature ($T = Cte$):

The left diagram in the set of diagrams below, shows isothermal expansion. In this case, the **expansion** comes with a **decrease in pressure** from p_1 to p_2 and a **volume increase** from V_1 to V_2 .

The right diagram in the set of diagrams below, shows **isothermal compression**, and the inverse process occurs: the **volume decreases** from V_1 to V_2 and the **pressure increases** from p_1 to p_2 .

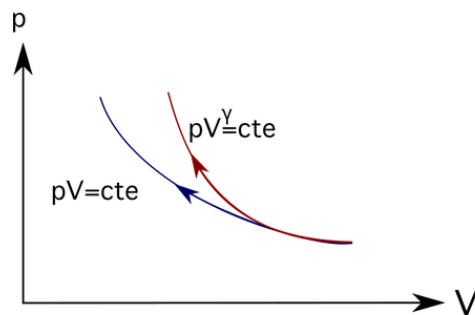


4. Adiabatic – no heat flows in and out of the container ($Q = 0$) :

PV diagrams for adiabatic processes are similar. In this case, **adiabatic processes** follow this equation:

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

Because of this equation, the processes form a **much steeper curve** (see the image below). In PV diagrams, the main difference between isothermals and adiabats (lines in adiabatic processes) is their steeper slope. In this process, **expansion and compression follow the same behaviours as isothermals**.



IV- state and Path function in Thermodynamics :

The state of a system is determined with the help of some measurable quantities like volume, temperature, density, pressure, etc. These quantities that can identify the state of a function are called properties. State and path functions both are *thermodynamics terms* that are used to name these properties.

IV-1- State function in Thermodynamics :

A *thermodynamic property that depends only on the initial and final state* and does not depend on the path taken to reach the final state or value is ***known as the state function*** or point function.

Properties that depend on state include pressure, temperature, amount of substance, etc. For example, density is a state function, it does not depend on how a substance is obtained. Similarly, the thermodynamics properties like internal energy (U), enthalpy (H), entropy (S), etc., are state functions. A change in their values depends on their initial and final state.

The state functions depend on the values of different parameters at a particular time, it does not depend on how these values are obtained or irrespective of the path taken.

Let us take a ***simple example to understand state function;***

A person standing on the first floor of a building. His potential energy is mgh_1 where m is the mass of the person, g is gravity and h_1 is the height of the first floor from the ground. Now he reaches the top floor by lift then his potential energy becomes mgh_2 where m (mass) and gravity (g) are the same only height changes. Now if he takes a different route to reach the top floor such as stairs even then the potential energy will be mgh_2 as he reaches the same height in this case. So, the potential energy depends on the initial and final heights irrespective of the path followed to reach the top floor. So, potential energy is a state function, not a path function.

IV-2- Path function in Thermodynamics :

A *thermodynamic property that depends on the path between the initial and final state is known as the path function*. The path functions depend on the path taken or covered between two (initial and final) states. For example, work and heat. If different paths are chosen to reach from one point to another point, the work done will be different however you reach the same point in each case. So, work is not a state function as we cannot say that a system will have a specific amount of work at a specific state.

Let us take a ***simple example to understand path function;***

Path function is a thermodynamic property whose value depends on the path followed to attain that value. For example, a person carries a 10kg weight from point A to point B after travelling a distance of 2 km and the work done by him is W . In this second case, he takes the same weight from point A to point B but this time he travels 3 km, so in this case, the work done by him will be more, however, he takes the weight to the same destination. So, we can see the work done

by him depends on the path followed, so, work is a path function. A path function has variable values based on the route.

IV-3- Difference between state function and path function :

State Function	Path Function
It refers to a property whose value does not depend on the path followed to reach that value.	It is a property whose value depends on the path followed to reach that value.
They are also called point functions.	They are also called process functions.
It can be integrated using values of the initial and final state of a system.	They need multiple integrals and limits of integration for integrating the property of the system.
Value of state function remains the same regardless of the path or steps involved to reach that value.	Value of the path function will be different if a different path is taken to reach the final state.
Different paths give the same value	Different paths give different values
For example; entropy, mass, temperature, volume, etc.	Example; heat and mechanical work.

V- Evolution and thermodynamic equilibrium states of a system :

V-1- Equilibrium states of a system :

The system is in a state of thermodynamic balance when the values of state variables are constant at each point of the system and remain constant over time.

V-2-Evolution states of a system :

The system's transition from a primary to a final state as a result of a change in the value of the state variables is called a transformation and is in two ways either reversible or irreversible:

V-2-1- Reversible transformation :

A thermodynamic process (state $i \rightarrow$ state f) is said to be reversible if the process can be turned back to such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. As we know, in reality, no such processes as reversible processes can exist. Thus, reversible processes can easily be defined as idealizations or models of real processes on which the limits of the system or device are to be defined. They help us in incurring the maximum efficiency a system can provide in ideal working conditions and, thus, the target design that can be set, example : slow adiabatic compression or expansion of gases

V-2-2- Irreversible transformation :

An irreversible process can be defined as a process in which the system and the surroundings do not return to their original condition once the process is initiated. Take an example of an automobile engine that has travelled a distance with the aid of fuel equal to an amount 'x'. During the process, the fuel burns to provide energy to the engine, converting itself into smoke and heat energy. We cannot retrieve the energy lost by the fuel and cannot get back the original form. There are many factors due to which the irreversibility of a process occurs, namely:

1. The friction that converts the energy of the fuel to heat energy
2. The unrestrained expansion of the fluid prevents from regaining the original form of the fuel Heat transfer through a finite temperature, the reverse of which is not possible as the forward process, in this case, is spontaneous
3. Mixing of two different substances that cannot be separated as the intermixing process is again spontaneous in nature, the reverse of which is not feasible.

Thus, some processes are reversible while others are irreversible in nature, depending upon their ability to return to their original state from their final state.