Chapter 1

Basics concepts of Thermodynamics

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, has been set forth.

II. Basic concepts and definitions:

1. Thermodynamic system: 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.

2. Surrounding: Is a special type of a system that has a very large size. The system under consideration can change its state as a result of its contact to the bath but the state of the bath does not change due to the interaction with a much smaller system. For instance, the thermometer measuring the temperature of a body can be considered as the system, whereas the body itself plays the role of the bath.

3. Boundary: The real or imaginary surface that separates the system from its surroundings. The boundaries of a system can be fixed or movable. Mathematically, the boundary has zero thickness, no mass, and no volume.

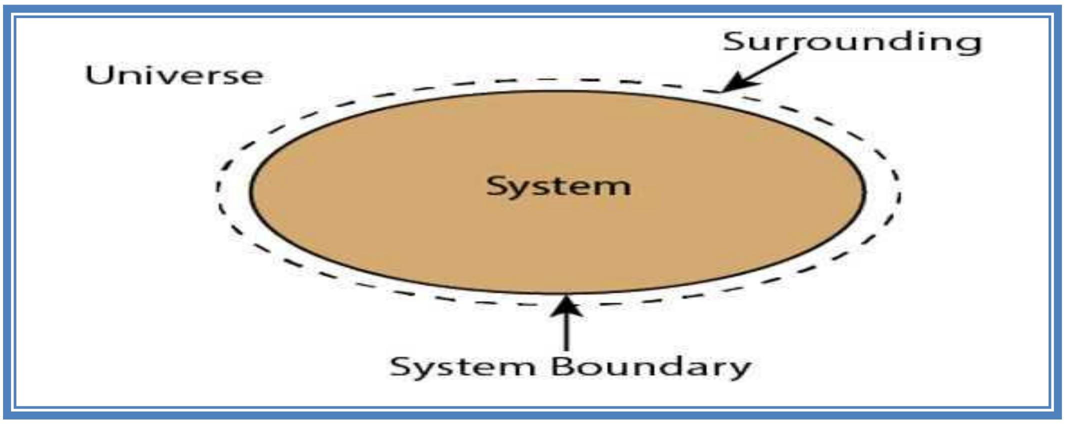


Figure 1

Example:

In Figure 2 the gas in the cylinder is considered to be the system. When the cylinder is heated from below, the temperature of the gas will increase and the piston will rise. As the piston rises, the boundary of the system moves. Heat and work cross the boundary of the system during this thermodynamic process, but the matter that comprises the system can always be identified.

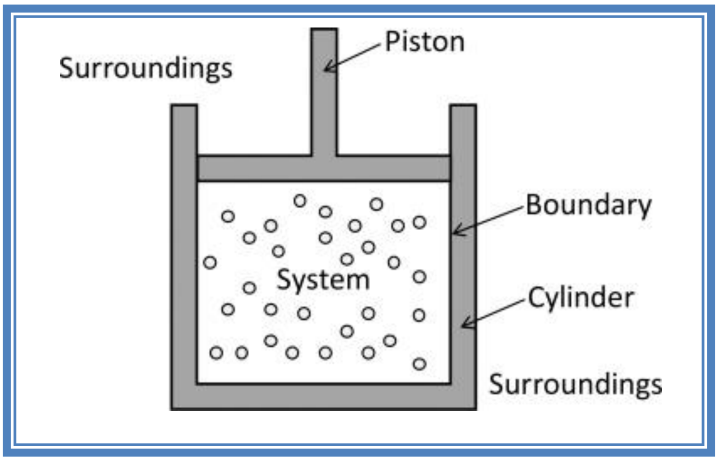


Figure 2

III. Types of systems in thermodynamics:

- **Closed system** or **control mass:** consists of a fixed amount of mass, and no mass can cross its boundary. But, energy in the form of heat or work, can cross the boundary, and the volume of a closed system does not have to be fixed.
- **Open system** or **control volume:** is a properly selected region in space. It usually encloses a device that involves mass flow such as a compressor. Both mass and energy can cross the boundary of a control volume.
- **Isolated system:** A closed system that does not communicate with the surroundings by any means.
- **Rigid system:** A closed system that communicates with the surroundings by heat only.
- **Adiabatic system:** A closed or open system that does not exchange energy with the surroundings by heat.

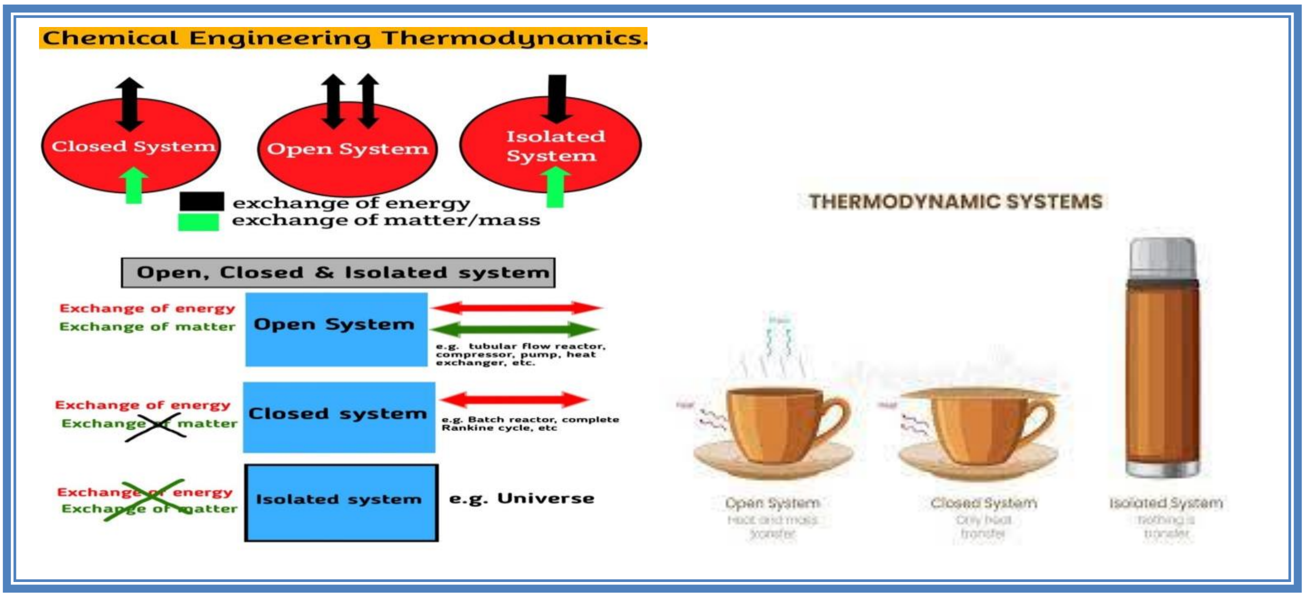


Figure 3.

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**).

VI. State of 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. Macroscopic physical quantities can be intensive and extensive.

- **Intensive quantities** (pressure P, temperature T) do not depend on the size (mass) of the system.
- **Extensive quantities** (mass M, volume V, energy E or U) scale with the system size.

To make this definition more precise, one can split the system into two equal parts by an imaginary membrane. The intensive quantities of the two resulting systems will remain the same while the extensive quantities of each subsystem will be half of that for the whole system. Specific quantities are the third type of quantities that can be obtained from an extensive quantity by division by another extensive quantity. By this definition, specific quantities do not depend on the system size. An example of specific quantity is the mass density.

V. Definition of certain thermodynamic variables:

V. 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):

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

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

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

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

V-2- Notion of temperature: Temperature is a measure of how hot or cold an object or system is. Temperature scales: centesimal, absolute and Fahrenheit.

- **Centesimal:** Its unit is the degree Celsius (°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.
- **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.
- **Fahrenheit:** Its unit is the degree Fahrenheit (°F). It is expressed by the relation: At 32 °F ice melts and at 212 °F water boils.

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

$$T(°\text{F}) = 1.8\ T\ (°\text{C}) + 32$$

V-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)...

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

V-4- Regular condition and standard condition:

- ✓ **Regular ambient temperature and pressure(SATP)**

T = 25 °C = 298.15 K

P = 1 atm

- ✓ **standard temperature and pressure (STP)**

T = 0 °C = 273.15 K

P = 1 atm

VI- Ideal 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.

VII-Ideal gas laws: The perfect gas rigorously obeys the three laws: MARIOTTE, GAY LUSSAC and CHARLES.

VII-1- Boyle-MARIOTTE 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 : $P.V = n.R.T$; $T = Cte \Longrightarrow P.V = Cte \Longrightarrow V \alpha 1/P \Longrightarrow$ **$P=Cte/V$**

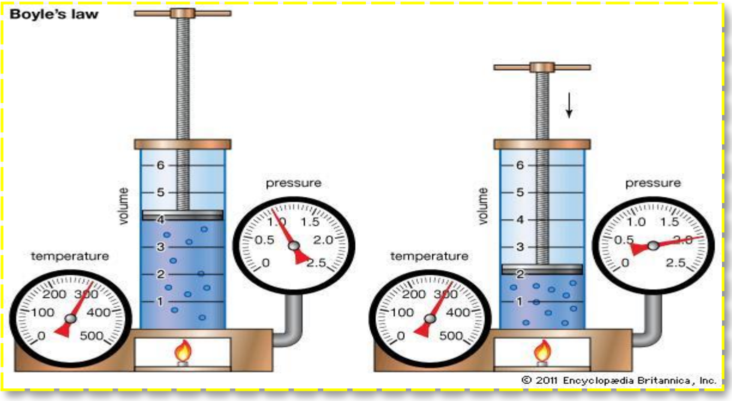


Figure 4.

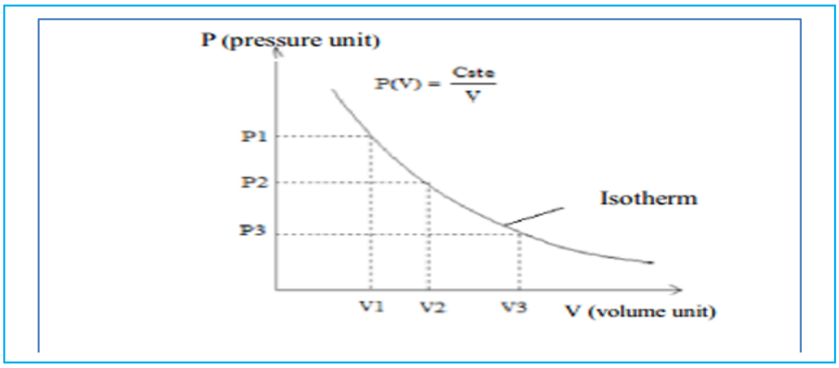


Figure 5.

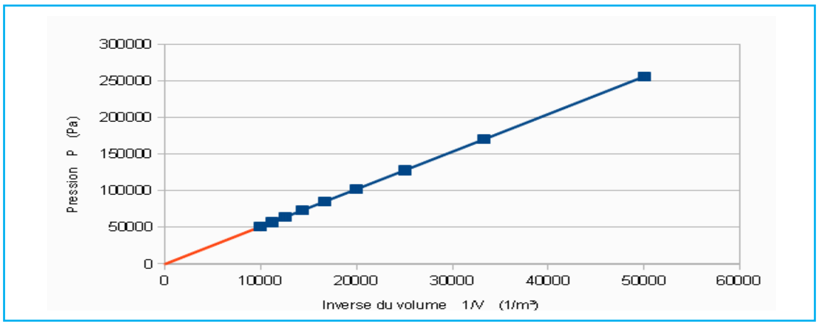


Figure 6.

$$V \propto 1/P \Longrightarrow V=K\times 1/P \Longrightarrow P\times V= K(Cte)$$
$$\Longrightarrow P_1 V_1 = P_2 V_2=P_n V_n$$

VII- 2- GAY-LUSSAC law: At constant volume, the pressure of a quantity of gas is directly proportional to its temperature.

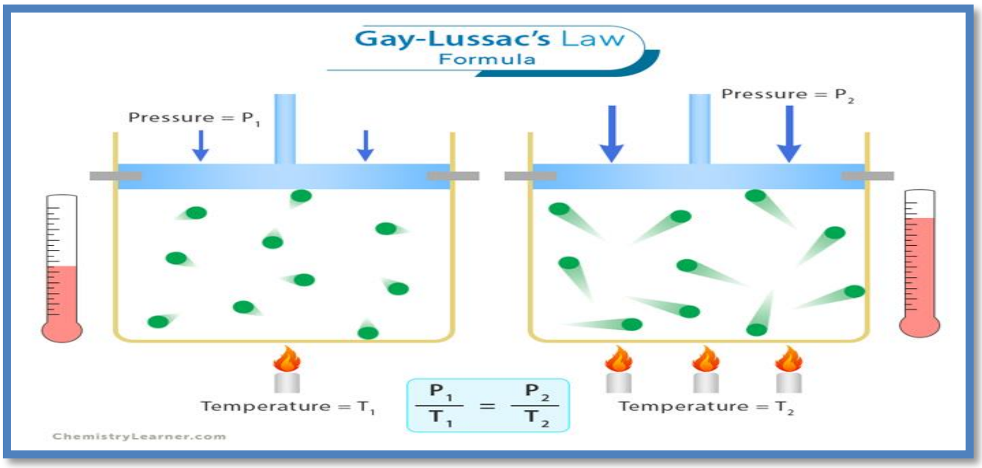


Figure 7.

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

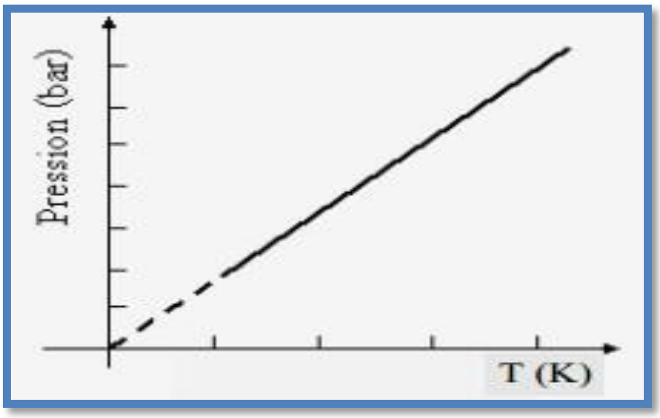


Figure 8.

VII- 3- CHARLES law: 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 $\Longrightarrow$V= $\frac{nRT}{P}$ = Cte. T$\Longrightarrow$ V $\propto$ T

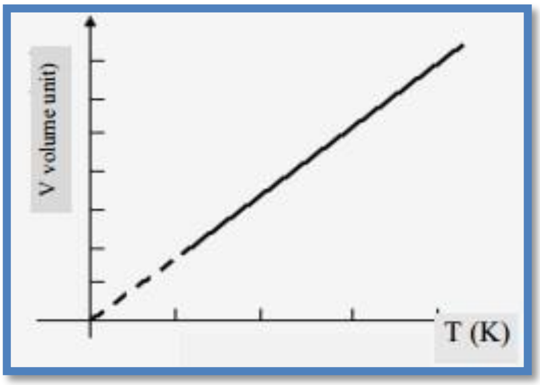


Figure 9.

VII- 4- Afogadro'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.

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

VIII- 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: $V \propto T$

Avogadro Law: $V \propto n$

According to the laws of proportionality in mathematics:

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

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 :

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

$$P = 1\text{atm} = 1{,}01325.10^5\ \text{Pa}; V = 22{,}4\ \text{l} = 22{,}4\ .10^{-3}\text{m}^3; T = 0 + 273{,}15\ \text{K};$$

$$n = 1\ \text{mole} \Rightarrow R = \frac{1{,}01325.10^5 \times 22{,}4.\ 10^{-3}}{1 \times 273{,}15} \Rightarrow R = 8{,}314\ \text{J.mol}^{-1}.\text{K}^{-1}$$

R = 8.314 J/mol. K

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

R = 2 cal/mol. K

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

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

R = 0,082 l.atm/mol.K

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

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

Where p_1, p_2, ..., p_n represent the partial pressures of each component.

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

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): $xi = \frac{ni}{\text{ntot}}$

It is denoted $\boldsymbol{x_i}$ (lowercase Roman letter *x*), sometimes $\boldsymbol{\chi_i}$ (lowercase Greek letter chi). (For mixtures of gases, the letter *y* is recommended.)

VIII-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.

VIII-1- Types of PV Diagrams: We can associate four general thermodynamic processes with the container-piston system above.

- **Isobaric (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).

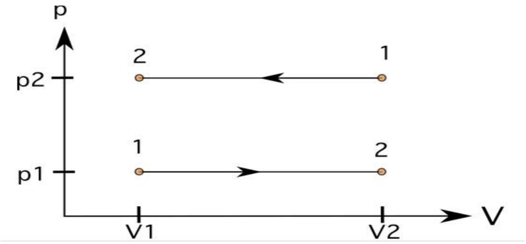


Figure 10.

- **Isochoric (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.

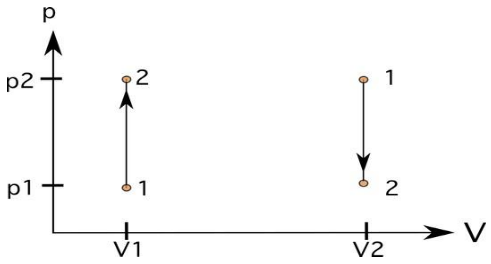


Figure 11.

- **Isothermal (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.

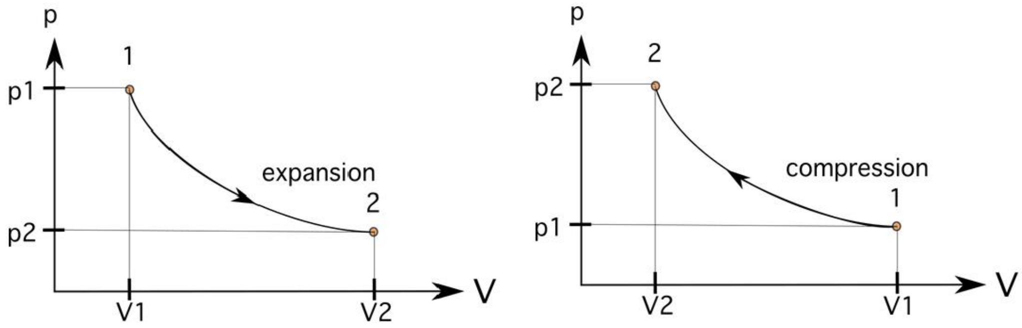
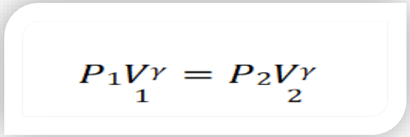


Figure 12.

- **Adiabatic (Q = 0)** :PV diagrams for adiabatic processes are similar. In this case, **adiabatic processes** follow this equation:



$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

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 behaviors' as isothermals.**

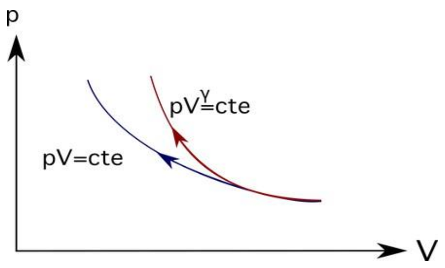


Figure 13.

VIIII-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:

- ✓ **Reversible transformation:** A thermodynamic process (state i ⟶ 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.

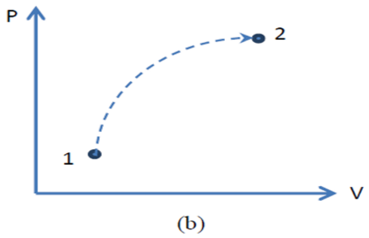
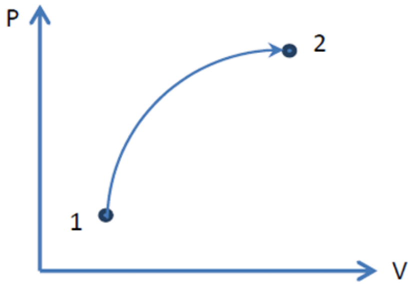


Figure 14.

- ✓ **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.

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.



(a)

Figure 15.