Chapter I

Basic concepts in thermodynamics

I-Introduction:

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, entropy, and the physical properties of matter and radiation. The behavior of these quantities is governed by the four laws of thermodynamics, which convey a quantitative description using measurable macroscopic physical quantities but may be explained in terms of microscopic constituents by statistical mechanics.

Thermodynamics applies to various topics in science and engineering, especially physical chemistry, biochemistry, chemical engineering, and mechanical engineering, as well as other complex fields such as meteorology. In thermodynamics, interactions between large ensembles of objects are studied and categorized. Central to this are the concepts of the thermodynamic system and its surroundings. A system is composed of particles, whose average motions define its properties, and those properties are in turn related to one another through equation of state.

II-Mathematical review of partial derivatives:

A partial derivative is a derivative of a function with more than one variable, where you change one variable only and keep the others constant.

Example: $f(x, y) = x^2 + xy$

- Partial derivative with respect to x:

$$\frac{\partial f}{\partial x} = 2x + y$$

- Partial derivative with respect to y:

$$\frac{\partial f}{\partial y} = x$$

II-1.How to compute partial derivative?

Differentiate like in one variable, and ignore the other variables.

Example: $f(x, y) = 3x^2y + 5y$

- *With respect to x:* $\frac{\partial f}{\partial x} = 6xy$

- *With respect to y:* $\frac{\partial f}{\partial y} = 3x^2 + 5$

II-2.Function of three variables:

If $f(x, y, z)$ you can compute $\frac{\partial f}{\partial x}; \frac{\partial f}{\partial y}; \frac{\partial f}{\partial z}$

Example: $f(x, y, z) = x^2y + yz$

$\frac{\partial f}{\partial x} = 2xy; \frac{\partial f}{\partial y} = x^2 + z; \frac{\partial f}{\partial z} = y$

II-3.Total differential:

If a quantity depends on two variables: $f = f(x, y)$ a small change in f is

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$$

This is just saying: ***change in f come from changes in x and y***.

Example: The volume of a cone depends on its radius and height with the relationship $V = \frac{h\pi}{3} r^2 \to V(r, h)$ so it is a function of two variables.

- *Partial derivative* ***V*** *with respect to* ***r***: $\frac{\partial V}{\partial r} = \frac{2}{3} h\pi r \to r^{\uparrow} \leftrightarrow V^{\uparrow}$
- *Partial derivative* ***V*** *with respect to* ***h***: $\frac{\partial V}{\partial h} = \frac{\pi}{3} r^2 \to h^{\uparrow} \leftrightarrow V^{\uparrow}$

$$dV = \frac{2}{3} h\pi r \, dr + \frac{\pi}{3} r^2 dh$$

The differentiation ***dV*** gave information about the volume when the radius and height were varied.

II-4.Used partial derivatives in thermodynamics:

In thermodynamics, one quantity depends on several others; example: pressure depends on temperature and volume P= P (T, V).

$\left(\frac{\partial P}{\partial T}\right)_V$ means how pressure change when change, while volume is kept constant.

$(\frac{\partial P}{\partial V})_T$ means how pressure change when volume change, while temperature is kept constant.

III-Properties and states of a system:

III-1.Thermodynamic system:

A thermodynamic system is a specific part of the universe, defined by a boundary (real or imaginary), that's isolated for study, focusing on matter and energy exchanges with its surroundings, governed by thermodynamics laws, and described by properties like temperature and pressure.

- ***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.
- ***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.

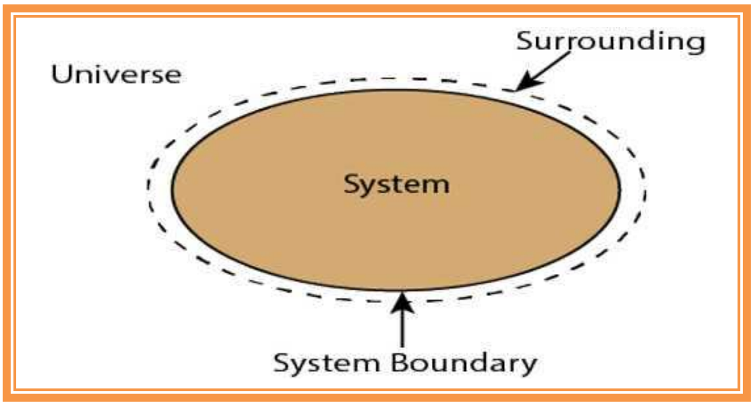

Figure 1: Thermodynamic system.

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.

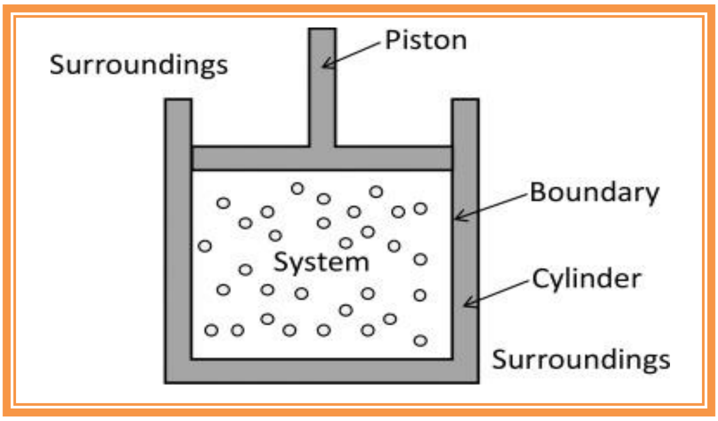

Figure 2: Example thermodynamic system

III-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.

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

c- ***Open system:*** is system that constantly exchanges both matter (mass) and energy with its surroundings.

Recap table

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

Examples:

- 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).**
- Liquid water boiling in a saucepan **(open system)**.
- When we boil water with a closed lid, the heat can exchange but matter cannot. **(Closed system)**.

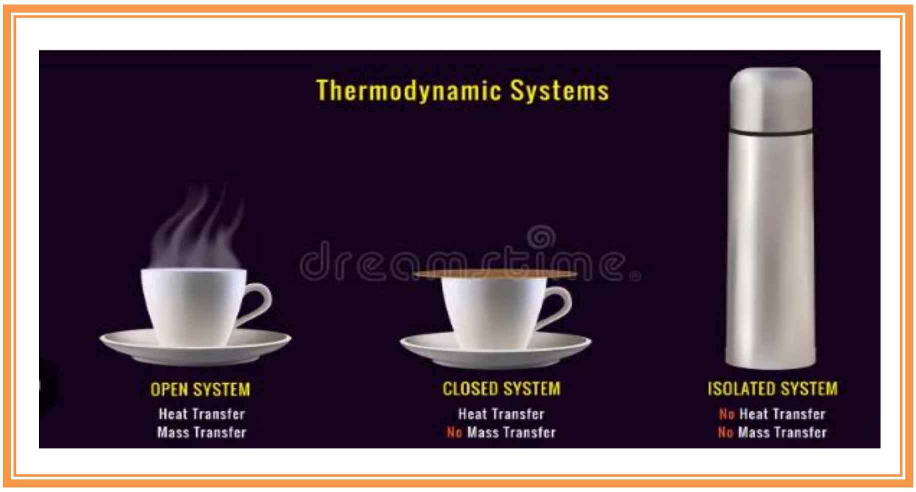

Figure 3: Example showing different types of systems

III-3.Properties of thermodynamic systems:

In thermodynamic, the properties of a system are the measurable or calculable characteristics that describe the state of the system. A property is any physical quantity that depends only on the state of the state of the system, not on how the system reached that state.

III-4.Classification of thermodynamic properties:

a- ***Intensive properties:*** Intensive properties are characteristics of matter that do not change with the amount or size of the substance, remaining constant regardless of how much you have. Key examples include *temperature, pressure, density, boiling/melting points, color, specific volume and hardness*, which help identify substances.

b- ***Extensive properties:*** Extensive properties are physical characteristics of a substance that depend on the amount of matter present, meaning they change if the sample size changes, like mass, volume. Key examples include *mass, volume, weight, enthalpy, entropy, and heat capacity*, all of which scale with the quantity of the substance.

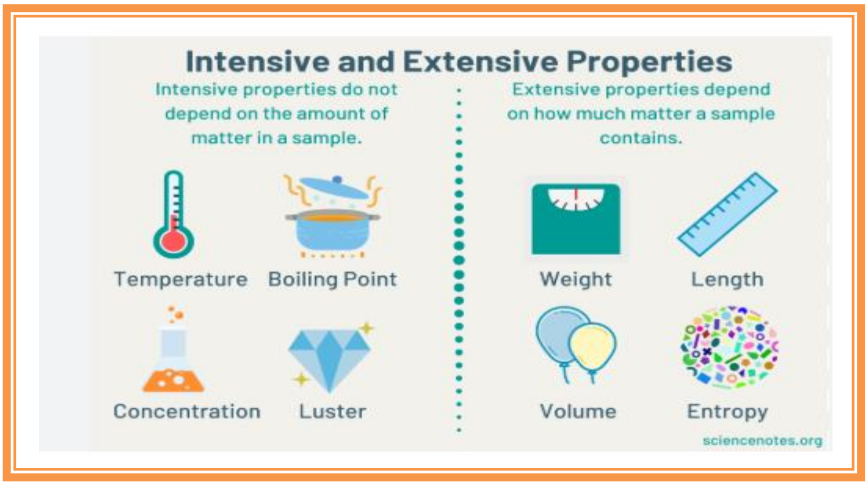

Figure 4: Intensive properties and Extensive properties

III-5.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 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 ; called the equation of state.

For a perfect gas: P.V - n R T = 0 or; P V = n RT

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

Table: the relationship between P, V and T

b-State variables

State variables in thermodynamics are measurable properties (like pressure (P), temperature (T), volume (V), internal energy (U), entropy (S), enthalpy (H), that completely define a system's condition at a given moment, independent of how it got there (Their values depend only on the system's current state, not the history or path taken to reach it), allowing us to understand and predict its behavior.

IV-Process, equilibrium and thermodynamic cycle:

IV-1.Thermodynamic process:

A process is the path or sequence of states a system traverses when moving from an initial state to a final state. While thermodynamic cycle is a series of processes where the system returns to its initial state, enabling work/heat conversion, like in engines or refrigeration.

IV-2.Types of Thermodynamic Processes:

- ✓ ***Isothermal process:*** is one in which the temperature of a system remains constant throughout the transformation (T=Cte). This process requires the system to exchange heat with its surroundings to maintain its temperature.
- ✓ ***Adiabatic process:*** is a key thermodynamic concept where a system changes state without any transfer of heat to or from its surroundings. This does not mean temperature remains unchanged; rather, any change in the system's internal energy comes only from work done, not from heat.
- ✓ ***Isobaric Process:*** Constant pressure (P). Volume may change; commonly seen when water boils in open vessels.
- ✓ ***Isochoric Process:*** Constant volume (V). Pressure or temperature may change; no work is done since $\Delta V = 0$.

IV-3.Representation of the thermodynamic process 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 result in a change in the other.

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

- ➢ **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.

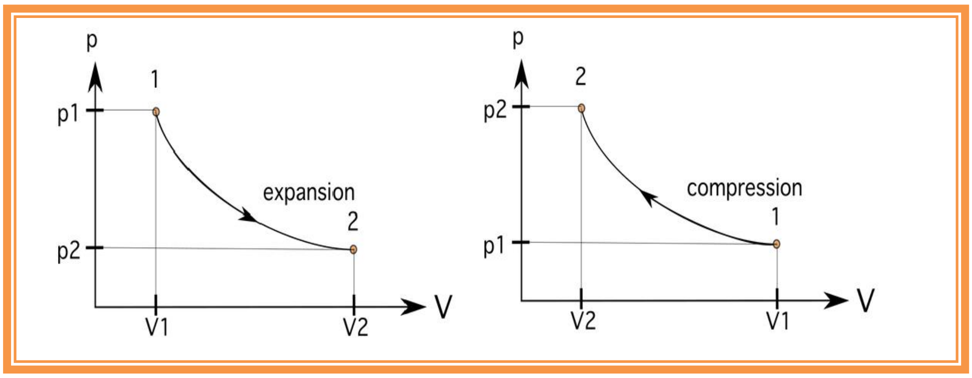

Figure 5: PV diagrams for isothermal processes.

- **Adiabatic (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 behaviors' as isothermals.**

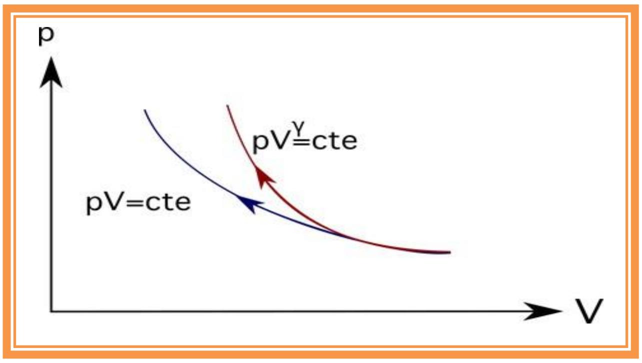

Figure 6: PV diagrams for adiabatic processes.

- **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).

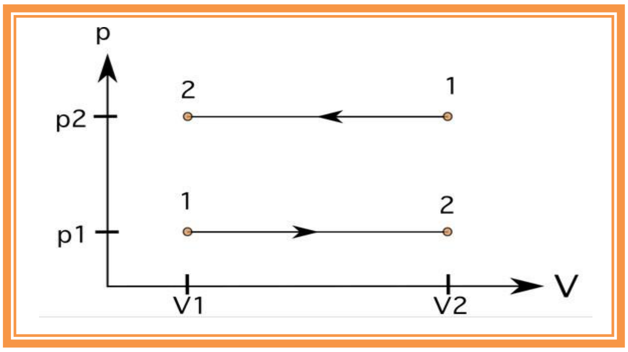

Figure 7: PV diagrams for isobaric processes.

- **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.

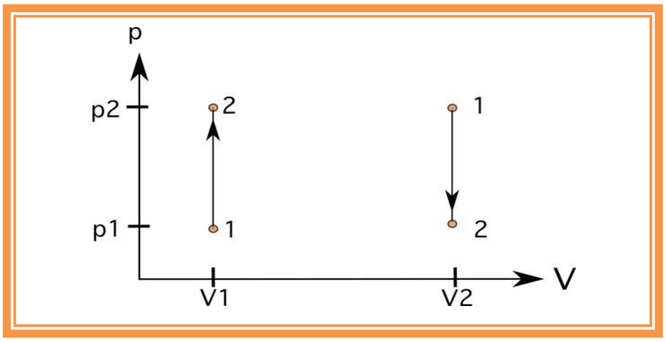

Figure 8: PV diagrams for isochoric processes.

- **Thermodynamic cycle:**

The concept of a thermodynamic cycle is based on depicting thermodynamic processes which involve the transfer heat and work. This is achieved by altering temperature, pressure, as well as other state variables; the cycle ultimately returns ing to its initial state. The fundamental basis of these cycles is the first law of thermodynamics which states that energy cannot be created nor destroyed but only converted from one form to another.

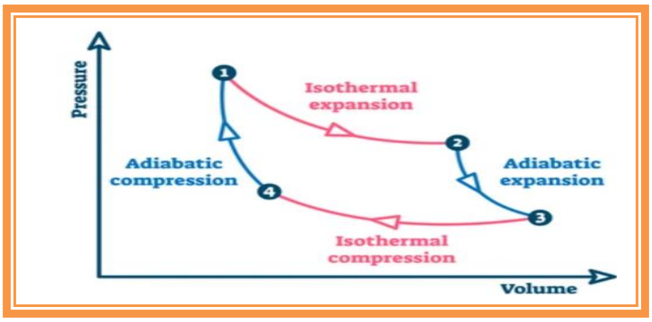

Figure 9: Thermodynamic cycle.

- ✓ ***Reversible and irreversible processes***

We shall find it useful to have in hand definitions for so-called reversible and irreversible processes.

- ***Reversible process:*** A process in which it is possible to return both the system and surroundings to their original states.
- ***Irreversible process:*** A process in which it is impossible to return both the system and surroundings to their original states.

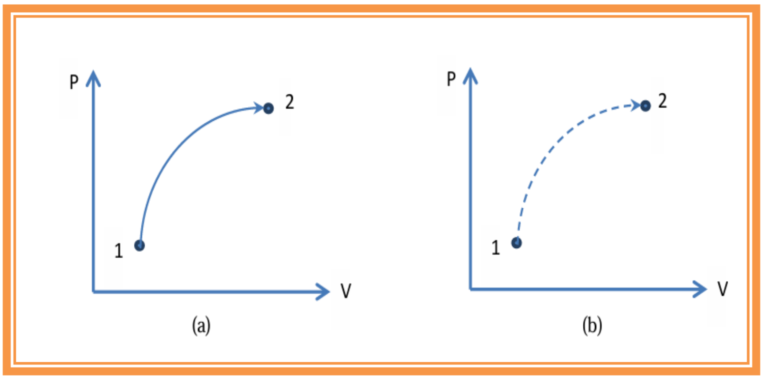

Figure 10: Reversible process and Irreversible processes

IV-3.Thermodynamic equilibrium: is a stable state where a system's properties (temperature, pressure, composition) are uniform and unchanging over time, meaning there's no net flow of energy or matter within the system or with its surroundings.

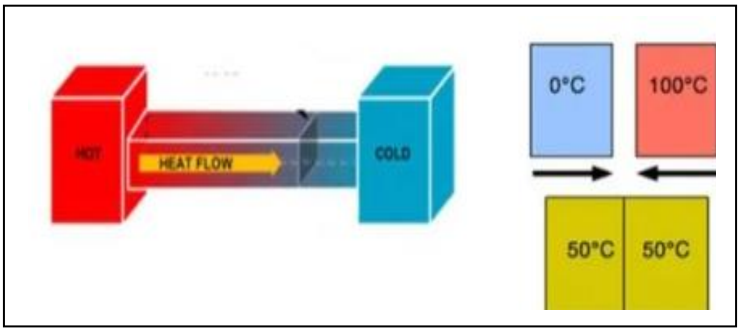

Figure 11: Thermal equilibrium.

V-Notion of density:

Density refers to how much mass is packed into a specific volume (mass/volume), indicating how compact or crowded something is. It's the ratio of an object's mass to its volume example: water's density is about 1 g/cm³.

$$d = \frac{m\ (mass)}{V(volume)}$$

VI-Notion of Specific volume:

The specific volume of a substance is defined as the volume per unit mass, and is given the symbol v:

$$v = \frac{\delta V}{\delta m} \ (m^3/Kg)$$

VII-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. *(N/m^2 or Pa)*

$$P = \frac{\delta F}{\delta A} \left(\frac{N}{m^2}\right) or \ Pa$$

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

1 Pa = 1 N/m^2 = 1 kg/ms^2

1 atm = 1.01325 . 10^5 Pa

1atm = 1.01325 Bar.

1 atm = 760 mmHg.

VIII-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.

Unit of 'T' (SI): K ; T(K) = T(°C) + 273

Standard Temperature and Pressure (STP): are reference conditions, most commonly **0°C (273.15 K)** and **1atmosphere (101.325 kPa)**, used in science especially chemistry, to compare gas properties like volume and density consistently.

Standard Ambient Temperature and Pressure (SATP): is a reference condition in chemistry and physics, defined as **25°C (298.15 K)** and **1 bar (100 kPa or 100,000 Pa)**, used for consistent gas measurements.

VIIII-Notion of energy:

One of the very important concepts in a study of thermodynamics is the concept of energy. Energy is a fundamental concept, such as mass or force and, as is often the case with such concepts, is very difficult to define. Energy is defined as the capability to produce an effect. It is important to note that energy can be stored within a system and can be transferred (as heat, for example) from one system to another.

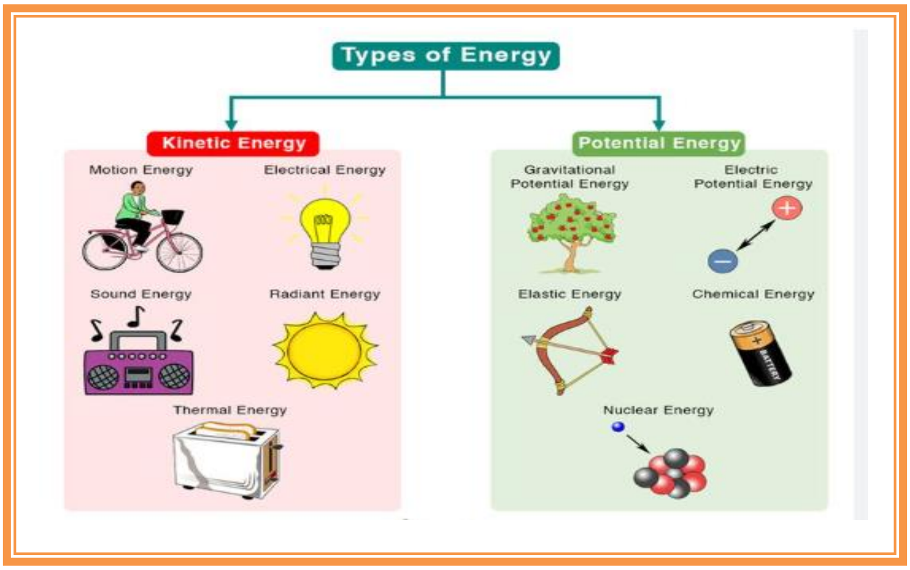

Figure 12: Types of energy.

Common energy units & Conversions:

The SI unit : Joule (J)

$1J= 1N.m=1Kg.m^2/s^2$

Calorie (cal): 1cal=4.184J

Erg: The CGS unit of energy: $1J=10^7$erg

1 L. atom = 24.23 cal = 101.3 J