Thermodynamics

III.1. Introduction

Thermodynamics studies the relationships between heat, work, energy, and transformations of matter. It is based on fundamental laws that describe the conservation and transformation of energy within systems. This discipline is essential for understanding numerous natural and technological phenomena (engines, refrigerators, biological processes, etc.).

III.2. Energy and Its Different Forms

Energy is the capacity of a system to perform work or to produce a change. It exists in different forms and can be converted from one form to another. The main forms of energy are:

1. **Kinetic energy:** Associated with the motion of an object (depends on mass and velocity), given by the equation:

$$E_{C\,tr} = \frac{1}{2} m\, v^2$$

2. **Potential energy:** Associated with the position or state of an object (e.g., gravitation, elasticity):

   a – Due to its position relative to the ground or relative to a reference level (a mass *m*, for example): In this case, potential energy is called **gravitational potential energy**, which can be defined by the equation:

$$U_{P\,m} = \pm\, m\, g\, h$$

   where *h* is the height of the object and ± denotes its position relative to the reference level (+ above and – below).

   b – Or due to its state: For example, a compressed or stretched spring. Potential energy is called **elastic potential energy**, given by the equation:

$$U_{P\,spring} = \frac{1}{2} k\, d^2$$

   where *d* is the deformation of the spring (the change in its length) and *k* is its stiffness (or spring constant).

3. **Thermal energy (or heat):** Associated with the agitation of molecules, transferred in the form of heat. It is given by the expression:

$$E_{th} = \frac{3}{2} k_B T = \frac{1}{2} m\, v^2$$

4. where k_B is the Boltzmann constant (1.381×10^{-23} J·K^{-1}) and v is the average velocity of the particles.
5. **Chemical energy:** This is the energy stored in the chemical bonds between atoms within a molecule. It is released when bonds form (bond energy) or absorbed when bonds break (dissociation energy), such as during combustion. In general, the stronger the bond, the higher the associated chemical energy. This energy is given by the expression:

$$\mathbf{\Delta E_{Bond} = E_{Products} - E_{Reactants}}$$

where $\mathbf{E_{Products}}$ is the total energy of the reaction products in eV, and $\mathbf{E_{Reactants}}$ is the total energy of the reactants in eV.

If $\mathbf{\Delta E_{Bond} < 0}$, it means that energy was released during the formation of bonds in the products, which is typically the case in **exothermic reactions**. Conversely, if $\mathbf{\Delta E_{Bond} > 0}$, energy was absorbed during bond formation, generally in the form of heat from the surroundings, which is the case in **endothermic reactions**.

6. **Electrical energy:** This is the energy associated with the movement of electric charges, generally electrons, through a conductor. It can be calculated using the following equation:

$$\mathbf{E_{elec} = P \cdot t}$$

Where: $\mathbf{E_{elec}}$ is electrical energy (in joules or kilowatt-hours); $\mathbf{P}$ is power (in watts or kilowatts); $\mathbf{t}$ is time (in seconds or hours).

7. **Nuclear energy:** This is the energy contained within atomic nuclei. It can be released during nuclear reactions, such as fission or fusion.
8. **Light (radiant) energy:** This is the energy carried by light. It is emitted by light sources and can be converted into other forms of energy, such as thermal energy.
9. **Mechanical energy:** This is the sum of the kinetic energy and the potential energy of a system. It is often used to describe the energy of a moving object. It is defined by the equation:

$$\mathbf{E_{mech} = E_C + U_P}$$

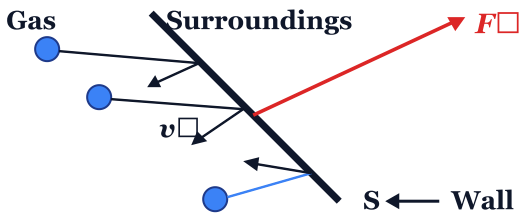
These different forms of energy can interact and transform into one another, according to the **principle of conservation of energy**, which states that the total energy of an isolated system remains constant.

III.3. Basic Physical Concepts

III.3.1. Concept of Temperature

Temperature: A measure of the degree of molecular agitation. It is related to the average kinetic energy of the particles. The Kelvin scale is used.

Example: A gas contained inside an enclosure. At the microscopic scale, the gas molecules move randomly throughout the enclosure with velocities around v_i, where v_i is the velocity of molecule i (or atom i).



Thus, temperature is defined by the following relationship:

$$EC = \frac{3}{2} k_B T = \frac{1}{2} m v^2 \quad \textbf{(average translational kinetic energy of the molecules)}$$

Where: **m** is the mass of the particles; **v** is the average velocity of the particles constituting the matter; $\mathbf{k_B}$ is the Boltzmann constant; **T** is the temperature of the matter.

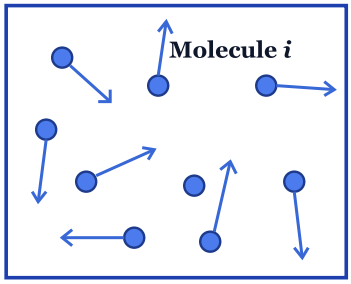
The absolute temperature scale (K) in Kelvin can be defined as a function of Celsius by:

$$T(K) = T(°C) + 273.15$$

III.3.2. Concept of Pressure – Kinetic Pressure

The pressure of a gas is caused by the numerous collisions of atoms or molecules of matter against the walls of the container. It is defined as the average force resulting from particle collisions on the walls per unit surface area:

$$P = \frac{F}{S}$$



Gas in an enclosure

Example: Inside the enclosure, there are N gas molecules in a volume V (equal to the volume of the enclosure) in constant agitation.

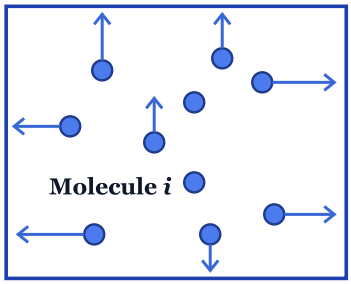
Let $n_V = \frac{N}{V}$ be the number of gas molecules in the enclosure per unit volume. Then, the kinetic pressure of the gas is defined by the following relationship:

$$\mathbf{P = \frac{1}{3} nVm\ v^2}$$

Where: **P** (in Pa = N/m^2) is the pressure of the gas inside the enclosure; **m** (in kg) is the mass of one gas molecule; **v** (in m/s) is the average velocity of the gas molecules. This can also be written as:

$$\mathbf{P \cdot V = \frac{1}{3} M\ v^2}$$

With: **M** (in kg/mol) being the molar mass of the gas (for 1 mole).



Pressure in an enclosure

III.3.3. Partial Pressure and Total Pressure – Dalton's Law

In a gas mixture, each gas exerts a partial pressure proportional to its mole fraction. The total pressure is the sum of the partial pressures.

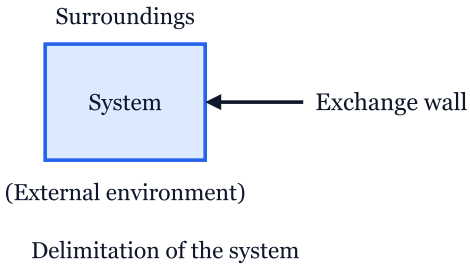
The total pressure of an ideal mixture of ideal gases is the sum of the partial pressures of each of its constituents. It is defined by the equation:

$$\mathbf{Ptot = \sum i Pi}$$

III.4. Thermodynamic Systems and Equilibrium States

III.4.1. Definition of a System

Thermodynamically, a **system** is a set of elements (a portion of matter under study) separated from the external environment (surroundings) by a boundary called a **wall**. The surroundings therefore constitute the rest of the space enclosing the system. Across the boundary (wall), exchanges of energy and matter (mass) may take place between the system and the surroundings.



Delimitation of the system

Exchanges of energy and matter occur in two possible forms: **heat (Q)** or **work (W)**.

Several types of thermodynamic systems are distinguished:

1. **Open system:** A system that exchanges both energy and matter with the surroundings; the wall is therefore called *permeable*;
2. **Closed system:** A system that exchanges only energy with the surroundings; the wall is therefore *semi-permeable* (impermeable to matter);

System	Matter Exchange	Energy Exchange	Example
Isolated	No	No	Calorimeter
Closed	No	Yes	Electric batteries
Open	Yes	Yes	Living organism

3. **Isolated system:** A system that makes no exchange with the surroundings—neither energy nor matter; the wall is therefore called *impermeable* (rigid and adiabatic). In an isolated system, total energy is constant.

III.4.2. State of the System

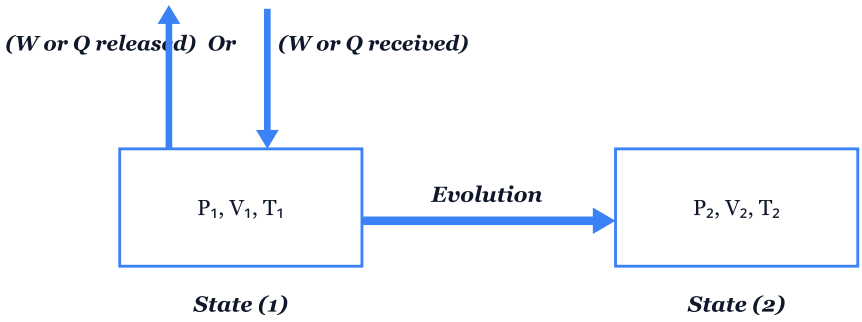
The state of a system is defined by macroscopic variables (*m, P, T, V*, etc.), also called **state variables** or **state parameters**. A system is said to be in a state of **thermodynamic equilibrium** if its state variables have well-defined and constant values. Several categories of variables are distinguished:

a – Thermal variables (*P, V, T*) or **calorific variables** (*U, H, W, Q, S*);

b – Extensive variables: Variables that depend on the amount of matter or the size of the system, such as (mass *m*, volume *V*, internal energy *U*, entropy *S*, etc.). These variables are additive when two systems are combined and change when the size of the system changes.

c – Intensive variables: Variables that are independent of the amount of matter or the size of the system, such as (density ρ, temperature *T*, pressure *P*, concentration, etc.). These variables are not additive when two systems are combined and remain constant.

III.4.3. Evolution or Transformation of the System



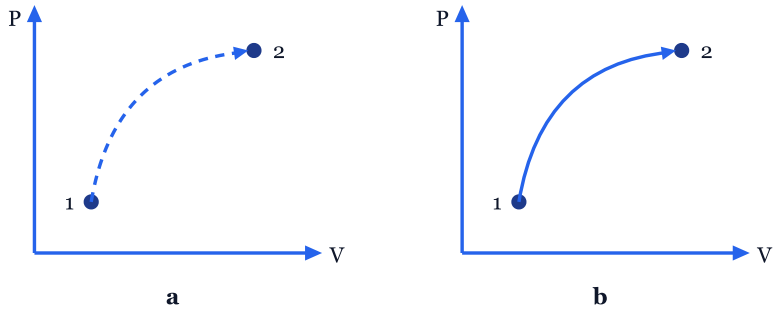
The **transformation** of a system is its passage from an initial equilibrium state (1) to a final equilibrium state (2). During this transformation, the system exchanges or transfers energy (*W* or *Q*) with the surroundings, either by receiving energy or by releasing it. In this case, the system is said to transform, evolve, or change state. The state variables of the system are therefore modified.

Transformation (evolution) of the system through exchange of energy (Q or W) with the surroundings.

During a transformation, the state variables of the system vary in order to reach another equilibrium state. The transition from equilibrium state (1) to equilibrium state (2) generally takes place out of equilibrium.

Two types of transformations are distinguished:

- **Reversible (or ideal) transformations:** Infinitely slow transformations consisting of a continuous succession of neighboring intermediate equilibrium states (*quasi-static*).
- **Irreversible (or real) transformations:** Rapid and sudden transformations whose intermediate states are not equilibrium states (*non-equilibrium*).



Transformations: a) – Reversible, b) – Irreversible.

III.4.4. Equations of State of the System

State variables are not all independent, but are linked together by equations called **equations of state** of the form:

$$f(P, V, T) = 0$$

Example:

The equation describing the behavior of a gas considered to be ideal is:

$$P\,V = n\,R\,T$$

Where: **P** is the pressure of the gas; **V** is the volume of the gas; **n** is the number of moles of the gas; **R** is the ideal gas constant; and **T** is the temperature of the gas.

In this equation, known as the **ideal gas equation of state**, each state variable (pressure, volume, or temperature) depends on the other two variables, namely: **P = f(T, V)**, **T = f(P, V)**, and **V = f(T, P)**.