1.1. Introduction :

The word thermodynamics is composed of two parts: "**thermo**" which means **heat** and "**dynamic**s" which means **movement**. The compound word means movement produced from heat.

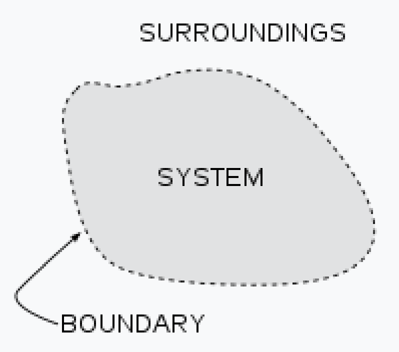
Thermodynamics aims to study the transfer of energy from one place to another and the possibility of its conversion from one form to another.

1.2. Definition of the thermodynamic system and the surroundings :

1.2.1. Definition:

A **thermodynamic system** is a set of substances confined in space by a **boundary** (wall). Everything outside the system to which energy or matter is exchanged is called its **surroundings (external environment)**. The system and the surroundings together make up the **universe**.

The universe = The system + The surroundings



1.2.2. Types of systems:

We distinguish three types of systems:

*** Isolated system:** Can not exchange either energy or matter with its surroundings. Example: the universe, calorimeter.

*** Closed system:** Can exchange energy but not matter with its surroundings. Example: electric batteries, internal combustion engine.

***Open system:** Can exchange both energy and matter with its surroundings. Example: living being, wood fire.

1.3. Description of a thermodynamic system:

1.3.1. Thermodynamic properties or variables :

The parameters or variables which are required to specify the state of the thermodynamic system are called thermodynamic variables, Examples : pressure, volume, temperature, number of moles......

1.3.2. Types of thermodynamic variables

***Intensive variables:** are independent of the mass (amount of matter). They are non-additive. Examples : Temperature, pressure, specific heat capacity, density.....

***Extensive variables:** depend on the mass (amount of matter). They are additive. Examples : Volume, mass, number of moles, entropy, heat capacity, enthalpy.....

1.3.3. State function:

***Definition :**

A state function is a mathematical relationship that links the thermodynamic variables of a system. Its change depends only on the initial and final states of the system and not on the path taken by the system.

***Mathematical properties of state functions:**

Let's consider a function of two variables x and y (F(x, y)). The differential form of this function is written:

$$\mathbf{dF = \frac{\partial F}{\partial x} |y \,.\, dx + \frac{\partial F}{\partial y} |x \,.\, dy}$$

$\frac{\partial F}{\partial x}$: 1st partial derivative of F with respect to x.

$\frac{\partial F}{\partial y}$: 1st partial derivative of F with respect to y.

The differential of a state function (dF) is an exact total differential (E.T.D); if :

$$\mathbf{\frac{\partial^2 F}{\partial x.\partial y} = \frac{\partial^2 F}{\partial y.\partial x}}$$

$\frac{\partial^2 F}{\partial x.\partial y}$: 2nd cross derivative of F with respect to y.

$\frac{\partial^2 F}{\partial y.\partial x}$: 2nd cross derivative of F with respect to x.

Example 1:

$F(x, y) = x^2 + y^2$

$\frac{\partial F}{\partial x} = 2x$ and $\frac{\partial F}{\partial y} = 2y$

$\frac{\partial^2 F}{\partial x.\partial y} = 0$ and $\frac{\partial^2 F}{\partial y.\partial x} = 0$

$\frac{\partial^2 F}{\partial x.\partial y} = \frac{\partial^2 F}{\partial y.\partial x}$; Therefore dF is ETD, hence: F(x, y) is a state function.

Example 2 :

$PV = nRT \longrightarrow V = \frac{nRT}{P} = V(P, T)$

$$dV = \left(\frac{\partial V}{\partial T}\right) dT + \left(\frac{\partial V}{\partial P}\right) dP$$

$\frac{\partial V}{\partial T} = \frac{nR}{P}$; and ; $\frac{\partial V}{\partial P} = -\frac{nRT}{P^2}$

$\frac{\partial^2 V}{\partial T\ \partial P} = -\frac{nR}{P^2}$; and ; $\frac{\partial^2 V}{\partial P\ \partial T} = -\frac{nR}{P^2}$

$\frac{\partial^2 V}{\partial T\ \partial P} = \frac{\partial^2 V}{\partial P\ \partial T}$; so; the volume is a fonction state.

1.4. Ideal gas equation of state :

*** Definition :**

An ideal gas is a theoretical gas whose molecules occupy negligible space (volume) and have no interactions.

***Ideal gas equation of state :**

The equation of state for ideal gases is given by: **PV = nRT**

With:

P: Gas pressure.
V: Gas volume.
T: Gas temperature.
n: number of moles of gas.
R: Ideal gas constant.

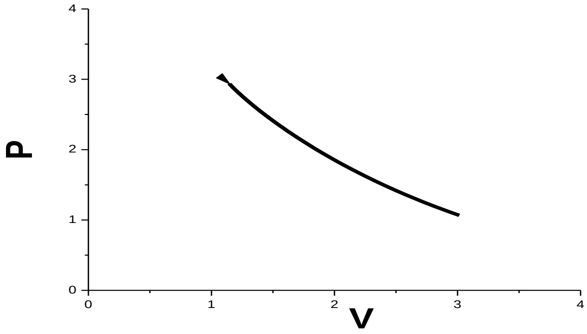
R = 0.082 atm.L/mol.K ; R = 8.314 Pa.m^3/mol.K ; R = 2 cal/mol.K

This equation of state combines the three laws obeyed by ideal gases :

A/ Law of BOYLE – MARIOTTE:

At constant temperature (T = constant), the volume of an ideal gas varies inversely with its pressure as follows:

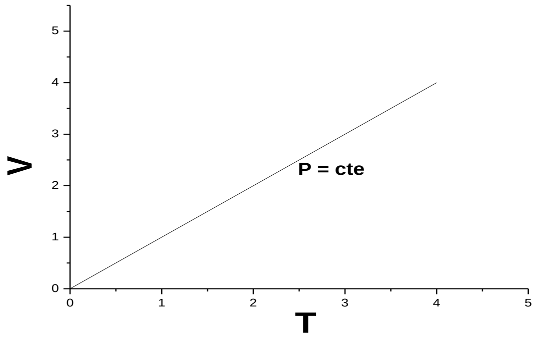
$$\mathbf{PV = Cte}$$



B/ Law of GAY – LUSSAC:

At constant pressure (P = constant), the volume of a gas is proportional to the temperature:

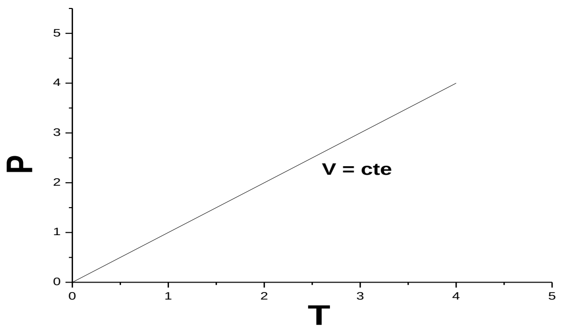
$$\mathbf{\frac{V}{T} = Cte}$$



C/ Law of CHARLES :

At constant volume (V = constant), the pressure of a gas is proportional to the temperature.

$$\mathbf{\frac{P}{T} = Cte}$$



D/ Law of Dalton (mixture of ideal gases):

Let's consider a mixture of several gases, contained in a volume $\mathbf{V_t}$, placed at a temperature **T** and subjected to a pressure $\mathbf{P_t}$.

*The application of the ideal gas law to the gas mixture gives: $P_t V_t = n_t RT$

*The application of the ideal gas law to each gas in the mixture gives: $P_i V_t = n_i RT$

With: $\mathbf{P_i}$ is the partial pressure of gas **i** (pressure exerted by gas **i** as if it was alone in the volume $\mathbf{V_t}$).

*Dalton's law defines that the total pressure exerted by a mixture of ideal gases is equal to the sum of the partial pressures of the constituents. $P_t = \sum_{i=1}^{n} P_i$

*We also have : $P_i = x_i . P_t$; with $x_i = \frac{n_i}{n_t}$ x_i: Mole fraction

1.5. Thermodynamic equilibrium :

Thermodynamic equilibrium is a state of a system in which there is no change occurs within the system over time. There are different types of thermodynamic equilibrium:

- **Thermal equilibrium:** The temperature of the system remains constant.
- **Mechanical equilibrium:** The pressure of the system remains constant.
- **Chemical equilibrium:** the chemical composition (concentration) of the system remains constant.

1.6. Possible transfers between the system and the surroundings :

The system interacts with its surroundings through:

***Mass transfer.**

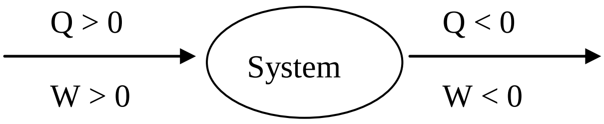
***Energy transfer** (in the form of **heat** (**Q**) and **work** (**W**)).

Sign convention:

*Everything received is positive.

*Everything that is lost is negative.

Work and **heat** are considered **positive** when the system receives them from the surroundings, and **negative** when the system loses them.



1.7. Transformations of the state of a system (Thermodynamic processes) :

Transformation is any modification of the system that leads to a final state different from the initial state. We distinguish:

***Isobaric transformation (Isobaric process):** occurs at constant pressure (P = constant).

***Isochoric transformation (Isochoric process):** occurs at constant volume (V = constant).

***Isothermal transformation (sothermal process):** occurs at a constant temperature (T = constant).

***Adiabatic transformation (Adiabatic process):** occurs without heat exchange between the system and the surroundings (Q = 0).

***Reversible transformation (Reversible process):** is a transformation in which the system and the surroundings return to their original states ($P_{int} = P_{ext}$).

***Irreversible transformation (Irreversible process):** is a transformation in which the system and the surroundings do not return to their original states ($P_{int} \neq P_{ext}$).

1.8. Physical and chemical transformations :

1.8.1. Physical transformation (Physical process):

Is a transformation that does not change the nature of the matter, during which chemical species are not modified. Example: change of state.

1.8.2. Chemical transformation (Chemical process):

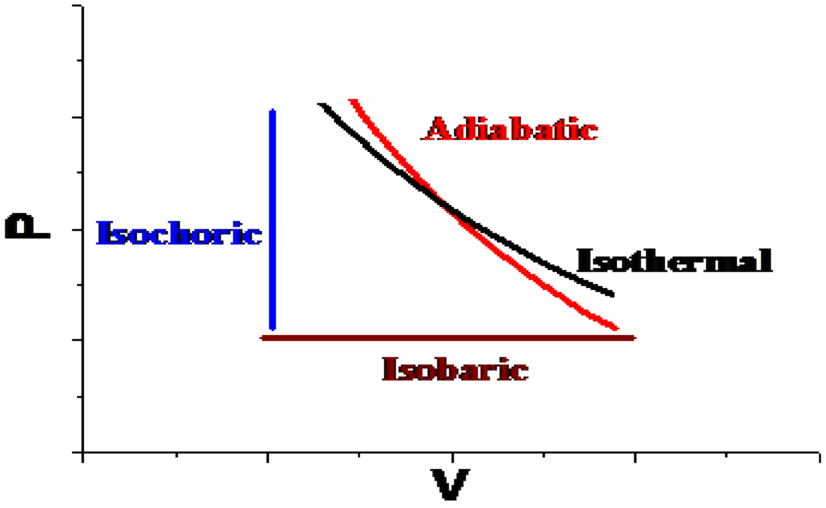
Is a transformation that changes the nature of matter, during which chemical species disappear (the reactants) and new chemical species appear (the products).

Example: Chemical reaction (Combustion reaction)

$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$

1.9. Clapeyron diagram:

It is a thermodynamic diagram representing, for a system, the variation of pressure as a function of volume P = f(V). Isothermal, isochoric, isobaric, and adiabatic transformations can be represented on the Clapeyron diagram (P, V).



1.10. Concept of temperature:

A/ Definition of temperature:

Temperature (T) is a measure of the average kinetic energy of the translational, vibrational, and rotational motions of matter's particles (molecules, atoms) in the system.

B/ Temperature scales:

***Celsius scale (Centigrade scale) :**

Noted **°C**. On this scale, the melting and boiling temperatures of water under atmospheric pressure (p = 1 atm) are: 0°C and 100°C, respectively.

***Kelvin scale (Absolute scale):**

Noted **K**. The melting and boiling temperatures of water correspond to 273.15 and 373.15 K at atmospheric pressure. 0°K corresponds to -273.15°C. The relationship between the Kelvin scale and the Celsius scale is given by:

$$\mathbf{T(K) = T(°C) + 273.15}$$

***Fahrenheit scale:**

Noted **°F**, on this scale the melting and boiling temperature of water under atmospheric pressure (P=1atm) are respectively 32 °F and 212 °F. The relationship between the Fahrenheit scale and the Celsius scale is given by: $\mathbf{T(°F) = 1.8\,T(°C) + 32}$

***Rankine scale:**

Noted **°R**. The relationship between the Fahrenheit scale and the Rankine scale is given by: $\mathbf{T(°R) = T(°F) + 459.67}$

1.11. Concept of pressure:

A/ Definition of pressure:

Pressure (P) is defined as the force exerted per unit area. **P=F/S**

B/ Pressure units:

*[P] : N. m^{-2} = Pa (Pascal)

*[P] : bar

*[P] : atm (Atmosphere)

*[P] : mmHg (Millimeter mercury)

*[P] : Torr (Torricelli)

1 atm = $1.01325.10^5$ Pa = 1.01325 bar = 760 mmHg = 760 Torr.

1.12. ZERO principle of thermodynamics:

« If two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other »