1.1. Introduction :

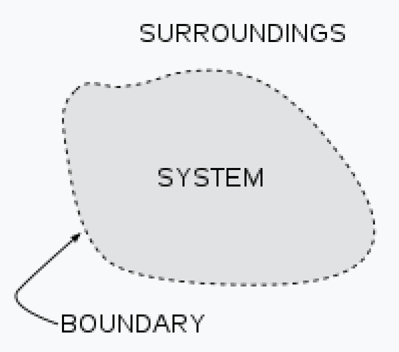
Thermodynamics is the science that aims to study the exchanges of energy that accompany changes in state and chemical reactions

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:

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

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

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

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

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

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

$\frac{\partial^2 F}{\partial y.\partial x}$: 2^{nd} 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.

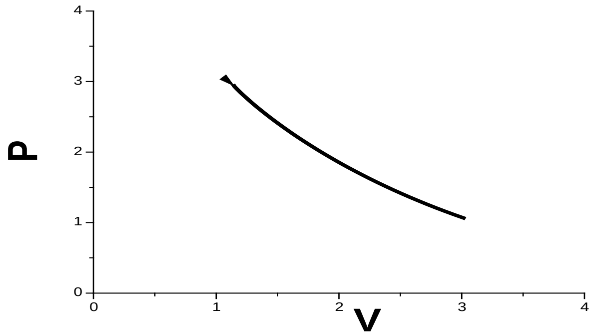
R = 0.082 atm.L/mol.K ; R = 8.314 Pa.m^3/mol.K ; R = 2 cal/mol.K

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:

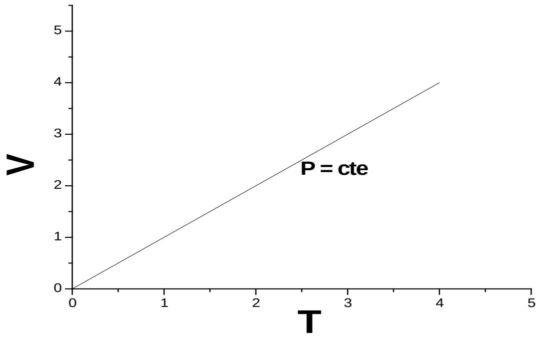
$$PV = Cte$$



B/ Law of GAY – LUSSAC:

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

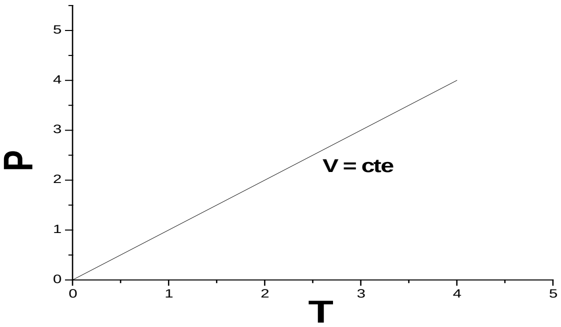
$$\frac{V}{T} = Cte$$



C/ Law of CHARLES :

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

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



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: $\mathbf{P_t V_t = n_t RT}$

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

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. $\mathbf{P_t = \sum_{i=1}^{n} P_i}$

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

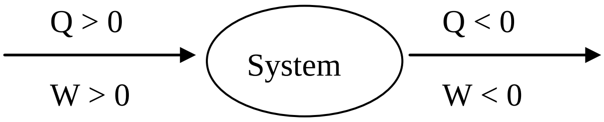
***Energy transfer** (in the form of **heat** (**Q**) and **work** (**W**)).

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):

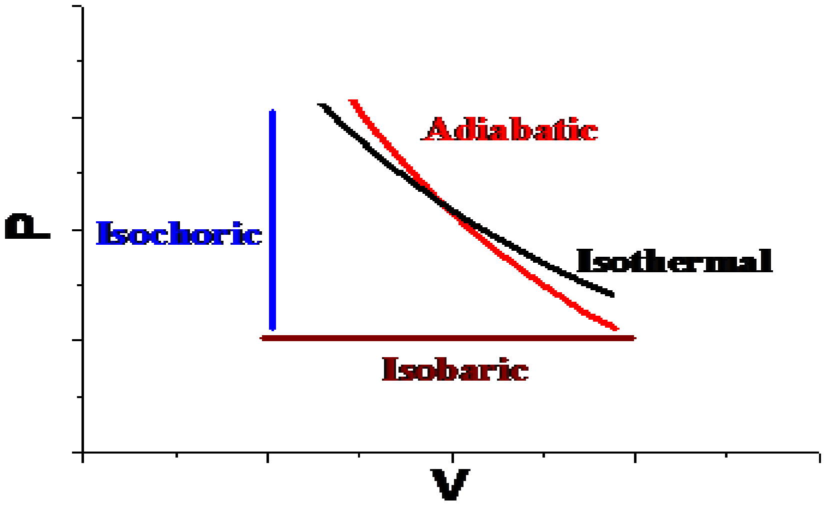
Is a transformation that changes the nature of matter, during which chemical species disappear (the reactants) and new chemical species appear (the products).

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 »