SOMMAIRE

Chapitre I

CHAPTER I: THERMODYNAMICS IN GENERAL

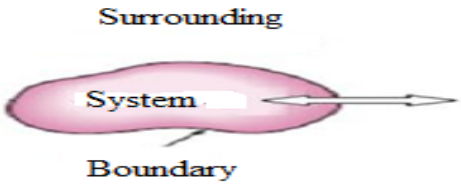
I. Introduction

The word thermodynamics is composed of two parts: "thermo" meaning heat and "dynamic" meaning work or movement. It is means movement produced from heat. Its aim is to study the different forms of energy and the possibilities of conversion between them: thermal energy ↔ mechanical energy, chemical energy,....etc.

II. Thermodynamic system

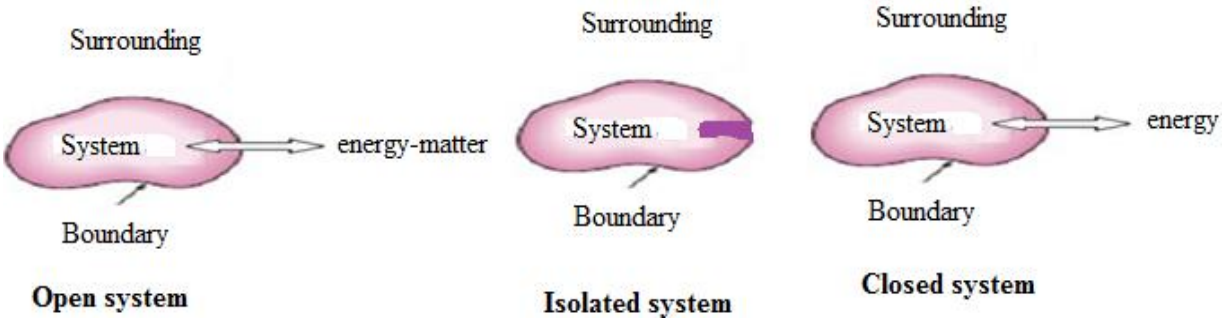
II.1. Concept of a system

The System is a finite portion of matter or a region in space with well defined boundaries which is selected to study. The rest of space outside the system is the surrounding.



On the basis of mass and energy transfer the thermodynamic system is divides into three types

- **Open system**: exchange of energy and matter with the external environment.
- **Isolated system**: no exchange of energy or matter with the external environment.
- **Closed system**: exchange only of energy with the external environment.



On the basis of composition of the system the thermodynamic system is divides into two types:

- **Homogeneous systems**: consist on single phase.
- **Heterogeneous systems**: is made up of several phases.

II.2. Description of thermodynamic system

II.2.1. State of a system and state variables

The state of a system is defined by the values of a number of proprieties known as state variables (or parameters). Exp: volume, pressure, temperature, viscosity, etc. These may be extensive (independent of the quantity of matter (are not additive: m, n, V) or intensive (dependent of the quantity of matter (are additive: T, P, M).

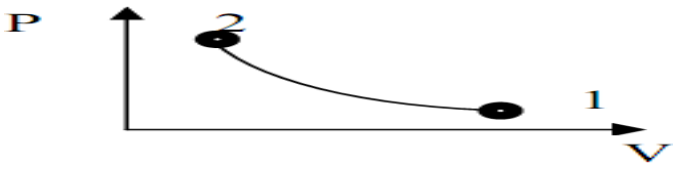
II.2.2. Thermodynamic equilibrium

A system is in thermodynamic equilibrium when all its state variables remain uniform (identical at all points in the system) and constant over time.

Thermodynamic equilibrium results from the conjunction of three equilibrium: thermal (temperature equality; T cst) mechanical (equal pressure, P cst) and chemical (equality of chemical potential).

II.2.3. Thermodynamic transformation

This is the passage from an initial state of equilibrium (1) to a final state of equilibrium (2), during which at least one state variable is modified.



a) Irreversible transformation

If, in the course of a transformation from an equilibrium state (1) to an equilibrium state (2), the successive intermediate states are not equilibrium states, the transformation is said to be irreversible. All real transformations are irreversible.

b) Quasi-static transformation

It is a transformation in which a system moves from one equilibrium state to another through a succession of equilibrium states. Such transformations can only take place infinitely slowly (since the equilibrium state must be reached at all times).

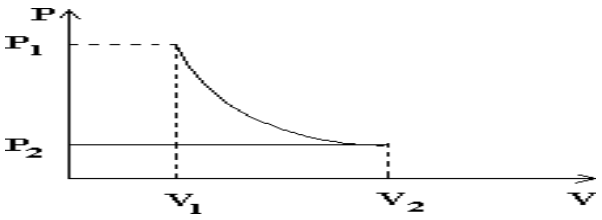
c) Reversible transformation

It is a transformation that can evolve in the opposite direction (reversible transformation) and passes through exactly the same intermediate equilibrium states for both the system and the external environment. In practice, a transformation can approach reversibility if it is carried out as slowly as possible, if friction is negligible, and if temperature differencesl.

d) Special transformations

- Isochoric transformations: V= constant.
- Isobaric transformations: P= constant.
- Isothermal transformations: T= constant.
- Adiabatic transformations: Q=0, transformations during which there is no heat exchange with the external environment.

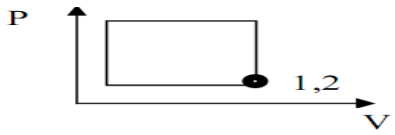
These transformations can be reversible or irreversible.



CLAPEYRON diagram (P, V).

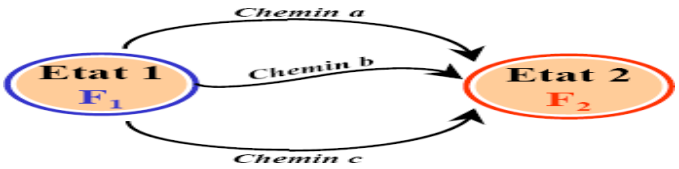
e) Closed transformations

A closed transformation is one in which the final state of the system is identical to the initial state (figure 2).



II.2.4. State function

Function F whose variation during a transformation depends only on the initial and final states and not on the path followed. Example: P, V, T ...



$\Delta F = F_{final} - F_{initial} = F_2 - F_1$ whatever the path followed: a, b, or c.

ΔF is independent of whether the transformation is carried out in a reversible or irreversible

Mathematical condition of a state function

The differential of a state function is an exact total differential DTE. This means that it is equal to the sum of its partial differentials with respect to each variable.

For a function of two variables denoted F(x,y):

$df = (\delta F / \delta x)\, dx + (\delta F / \delta y)\, dy$

$(\delta^2 F / \delta x\, \delta y) = (\delta^2 F / \delta y\, \delta x)$

III. Gas properties

III.1. Pressure

Pressure is defined as the force F exerted by a fluid on a surface element. The pressure of a gas is due to the shocks of molecules or atoms on the wall of the container containing the gas.

$$P = F/S \ (N/m^2) \text{ ou } (Pa)$$

Pressure units:

1 Pa (pascal, SI unit) = 1 N/m^2

1 atm= 1.01325 105 Pa = 1.01325 bar = 760 mmHg = 760 torr

II.2. Gase Laws

a. Boyle-Mariette's Law: At constant temperature, we have: P V = constant.

b. Gay-Lussac Law: At constant pressure, we have: VT= constant.

c. Charles's Law: At constant volume, we have: PT= constant.

d. Avogadro-Ampere Law: At constant pressure and temperature, we have: C = n/V constant.

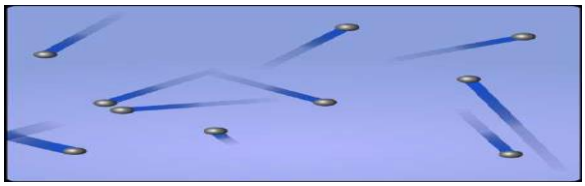
III.3. Equation of state perfect gas

Perfect gas is a theoretical model based on the following assumptions:

• There is no interaction between molecules (distant molecules);

• Molecules are assimilated to point masses;

• Shocks between molecules or against vessel walls are perfectly elastic.



$$PV = nRT$$

P: pressure of a perfect gas (Pa, atm, N/m^2)
1 atm = 1.013 105 Pa = 760 mm Hg = 76 cm Hg 1 bar = 105 Pa and N/m^2 = Pa
V: volume of a perfect gas (m^3, L)
n: The number of moles of the gas (mol)
T: temperature of the gas (K) T (K) = T (°C) + 273.15
R: Perfect gas constant.
In C.N.T.P (T = 0°C = 273.15K and P = 1 atm) one mole of a perfect gas occupies a volume V = 22.4 L
R = 8.314 Joul/mol K (P (Pa), V (m^3)) where Pa ×m3 = Joul
R = 0.082 L atm /mol K (P(atm), V (L))
R = 1.987 cal / mol K (1 cal = 4.18 Joul)

II.5. Mixing of perfect gases

a. Partial pressure:

In a mixture of several gases partial pressure of one of the gases is the pressure which would exert if it was the only one occupying the entire volume:

$$P_i = x_i P_T$$

$$\text{Mole fraction } x_i = n_i/n$$

$$\Sigma xi = 1$$

b. Dalton's Law:

A perfect gas mixture is itself a perfect gas. The pressure of a gas mixture is equal to the sum of the partial pressures:

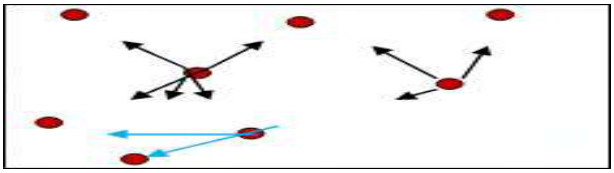
$$P_T = \Sigma Pi$$

c. Molar mass of perfect gas mixture:

$$M = m_T / n_T = \Sigma\, x_i M_i$$

II.6 Van Der Walls state equation: real gas:

In a real gas, interactions between molecules are no longer negligible and molecules are contain like radius spheres r.



$$[P + (n^2/V2)\, a)](V-nb) = nRT$$

a and b: characteristic of the gas.
b: covolume corresponding to the volumes of molecules not being punctual.
$(n^2/V2).a$: internal pressure due to interaction forces between molecules.