People's Democratic Republic of Algeria

Ministry Of Higher Education and Scientific Rfesfrearch

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<u>Course:</u>

Chemistry II (Thermodynamics)

This Chemistry II Handout (Thermodynamics) is particularly aimed at first year Common Base Science and Technology Engineer (ST) students. The content focuses on the three principles of thermodynamics and their applications, with a section on free enthalpy. The handout consists of seven chapters organized as follows:

- **Chapter I:** *Thermodynamics in general*
- **Chapter II:** *Heat, work and calorimetry*
- **Chapter III:** *First Principle of thermodynamics*
- **Chapter IV:** *Applications of the first principle of thermodynamics to Thermochemistry*
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CHAPTER I: Thermodynamics in general

Introduction :

The word thermodynamics is of Greek origin. It is made up of two parts: "thermo" meaning heat and "dynamic" meaning work or movement. The compound word means movement produced from heat. Thermodynamics emerged as a science in the *18thcentury*   with the discovery of the steam engine. Its aim is to study the different forms of energy and the possibilities of conversion between them. Thermodynamics has several branches:

- *Classical thermodynamics***:** studies systems on a macroscopic scale, using measurable quantities such as pressure P, temperature T and volume V.

- *Chemical thermodynamics***:** study of heats of reaction and thermodynamic properties of chemical equilibria.

- *Statistical thermodynamics:* takes into account systems in all their aspects microscopic aspects and is based on statistical mechanics.

*Technical thermodynamics***:** for thermal and refrigeration machines,heat pump. ect).

State of the art in thermodynamics :

- **1747:** Physiologist *A. HALLER* attributed the constant temperature of the humanbody to the friction that accompanies blood circulation.

- **1765**: *J. WATT* created the first steam engine with virtually no theoretical basis.

- **1824:** *S. CARNOT* formulated the second principle of thermodynamics, latercompleted (in **1848**) by *W. THOMSON* and *R. CLAUSIUS* (in **1850)**.

- **1842:** *R. MAYER* made the first statement of thermodynamics, which was confirmed by *J. JOULE* in **1845**.

- **1869:** *M. MASSIEU, J.W. GIBBS* (**1875)***, H.L.F. HELMOTZ (1882)*, and *P. DUHEM* **(1886)** formulated characteristic functions and thermodynamic potentials, andinitiated the application of thermodynamics to chemistry.

- **1877:** *L. BOLTZMANN* introduced statistical thermodynamics.

1. undamental properties of state functions :

The state of a system is described by a few macroscopic parameters called state quantities: volume, pressure, quantity of matter, temperature, etc. There are two such quantities:

- **Extensive quantities:** are defined for the system as a whole (volume, mass, energy, etc.), and are proportional to the quantity of matter in the system.

- **Intensive quantities:** are defined locally at each point of the system (density, pressure, temperature, etc.), and are independent of the quantity of matter in the system.

Reminder of mathematical definitions

Differential of a state function (¹ˢᵗ derivative and ²ⁿᵈ cross derivative)

Let f(x) be a function of a single variable x : The derivative of f is f' defined by :

$$f^{'} = \lim_{\Delta x \to 0} \frac{f(x + \Delta x) - f(x)}{\Delta x} = \frac{df(x)}{dx} \dots\dots\dots (I.1)$$

Or :

$$df^{'} = f^{'}(x)dx \Rightarrow df = \left(\frac{\partial f}{\partial x}\right)dx \dots\dots\dots (I.2)$$

Example:

Calculate the differential of the following function:

$$f(x) = 4x^2 + 2x + 5 \Rightarrow df(x) = (8x + 2)dx$$

Solution:

For a function f (x, y) with two variables x and y, the differential of f is defined by:

$$df(x, y) = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy.$$

$\left(\frac{\partial f}{\partial x}\right)_y$:⌐ is the derivative of f with respect to x for constant y.

$\left(\frac{\partial f}{\partial y}\right)_x$:⌐ is the derivative of f with respect to y for constant x.

Mathematical condition of a state function (D.T.E) :

The differential of a state function, a function of several independent variables, is an exact total differential (ETD). This means it is equal to the sum of its partial differentials with respect to each variable. For a function of two variables *F(x,y)* :

$$dF = \left(\frac{\partial F}{\partial x}\right)dx + \left(\frac{\partial F}{\partial y}\right)dy \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (I.3)$$

$\left(\frac{\partial F}{\partial x}\right)$: is the **partial derivative** of F with respect to x and the same for y.

The order of variation of the independent variables x and y has no effect on the result. This translates mathematically into the fact that the crossed second derivatives of the function F with respect to x and y are equal.

$$\frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (I.4)$$

Application example: (case of a perfect gas)

Consider a perfect gas whose state is given by its temperature **T** and pressure **P.** To carryout a transformation, the pressure or temperature of the gas is varied from initial values **Ti** and **Pi** to final values **T_f** and **P_f.**

The quantity of matter is considered constant

Volume case

The equation of state for the perfect gas gives us an explicit expression for the volume as a function of these two parameters:

$$V(T,P) = \frac{nRT}{P} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (I.5)$$

Volume therefore appears as a state function. From this expression, we can calculate the change in volume of the gas during the transformation from the initial to the final state:

$$\Delta V = V_f - V_i = nR \left[\frac{T_f}{P_f} - \frac{T_i}{P_i} \right] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (I.6)$$

The same variation can be verified by following two different transformation paths. For the first path, we vary the pressure from P_i to P_f, keeping the temperature constant and equal to T_i , then we vary the temperature from T_i to T_f, keeping the pressure constant and equal to P_f , then vice versa.

In the second path, we proceed in the same way, but vary the temperature before the pressure. For a small infinitesimal variation in pressure and temperature, we can write :

$$dV = \left(\frac{\partial V}{\partial T} \right) dT + \left(\frac{\partial V}{\partial P} \right) dP \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(I.7)$$

Using the equation of state :

$$dV = \frac{nR}{P} dT + \frac{nRT}{P^2} dP \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(I.8)$$

Consider the two different paths defined by the order of variation of P and T

- For the first path, we can write the total change in volume as follows, by first varying thepressure:

$$\Delta V_1 = \int_{Pi \to Pf : T=Ti} dV + \int_{Ti \to Tf : P=Pf} dV \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (I.9)$$

This gives :

$$\Delta V_1 = \int_{P \to Pi}^{Pf} -\frac{nRT_i}{P^2} dP + \int_{T \to Ti}^{Tf} \frac{nR}{P_f} dT \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(I.10)$$

$$\Delta V_1 = \left(\frac{nRT_i}{P_f} - \frac{nRT_i}{P_i} \right) + \frac{nRT}{P_f} \left(T_f - T_i \right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (I.11)$$

$$\Delta V_1 = V_f - V_i = nR \left[\frac{T_f}{P_f} - \frac{T_i}{P_i} \right] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(I.12)$$

For the second path, the temperature is varied first:

$$\Delta V_2 = \int_{Ti \to Tf : P=Pi} dV + \int_{Pi \to Pf : T=Tf} dV \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (I.13)$$

5

We find the same result as for the first path, which is obviously the same as that obtained directly from the equation of state. For the differential form **dV** of the function **V(T, P) to** be an exact differential, the order of the derivation of **V with** respect to **T** and **P** must be indifferent, or the crossed second derivatives must be equal, which is the case:

$$\frac{\partial^2 V}{\partial T \partial P} = \frac{\partial^2 V}{\partial P \partial T} = \frac{-nR}{P^2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(I.14)$$

Case of work

On the other hand, the work of the pressure forces depends on the path followed, so it cannot be written as the variation of a state function, and the work supplied during an infinitesimal transformation ∂W is not an exact differential.

We have already established the volume differential of a perfect gas:

$$dV = \frac{nR}{P} dT - \frac{nRT}{P^2} dP \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (I.15)$$

The work of pressure forces

$$\partial W = -PdV \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (I.16)$$

Therefore, the differential form of the work associated with a perfect gas is equal to :

$$\partial W = (-nR)dT + \left(\frac{nRT}{P}\right)dP\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(I.15)$$

We can show that ∂W is not an exact differential by noting that the crossed second derivatives are not equal.

$$\frac{\partial}{\partial P}(-nR) = 0 \neq \frac{\partial}{\partial T}\left(\frac{nRT}{P}\right) = \left(\frac{nR}{P}\right)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(I.16)$$

This is confirmed by calculating the work supplied during the transformation following the two different paths described above. For the first path, the work supplied is *w₁*.

$$W_1 = nRT_i \ln\left(\frac{P_f}{P_i}\right) - nR\left(T_f - T_i\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(I.17)$$

And for the second

$$W_2 = -nR(T_f - T_i) + nRT_f \ln\left(\frac{P_f}{P_i}\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(I.18)$$

The total work obtained in the two cases considered is different. It therefore depends on the pathfollowed and cannot be written as the variation of a state function.

2. Definitions of thermodynamic systems and the external environment

The system is a part of space (Universe) that we study. It is limited by a real or fictitious (arbitrary) surface through which exchanges of energy and/or matter take place with the external environment which is the rest of the universe

(Universe = system + external environment).

Fig.I.1: System and external environment [1,3
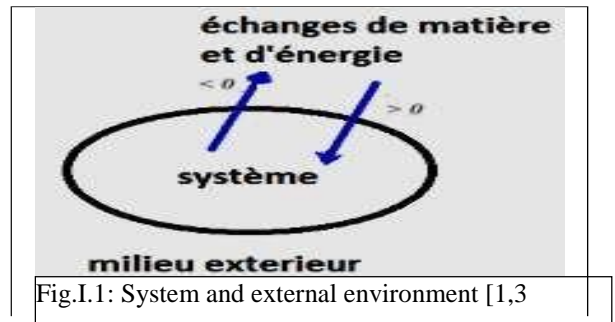
The constituents or composition of a system

Or again, the chemical system is a set of substances capable of evolving through transformations or chemical reactions during which the starting products or the products formed can undergo a change of state (vaporization, liquefaction, sublimation, fusion, etc.)

Different types of systems (open, closed, isolated)

Thermodynamics covers the following types of system:

OPEN SYSTEM

A system is open if it can exchange energy and matter with the outside world. Through its boundary.The exchange can be of energy (heat, work, etc.) or matter.

Example:

Gaz dans un récipient ouvert : peut subir une évaporation.   Fusée dont le combustible brule
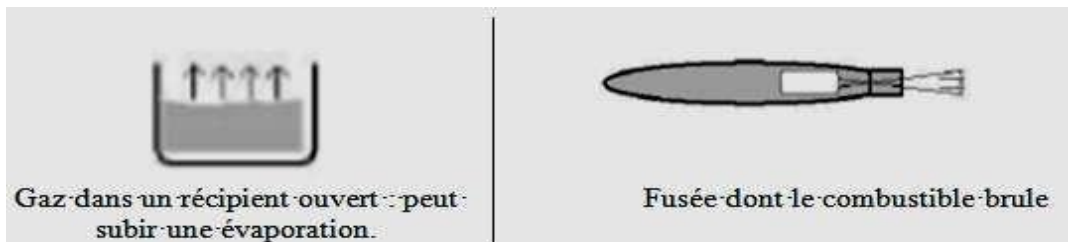
CLOSED SYSTEM

A system is closed if it allows a flow of energy with the outside environment, through its boundaries,but not mass.

Example:

Azote liquide dans un récipient fermé | écoulement d'eau : l'ensemble des deux bassins est fermé

ISOLATED SYSTEM
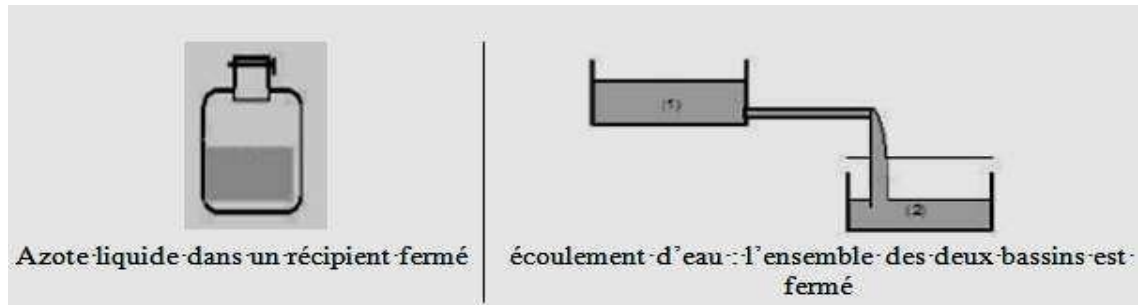
A system is said to be insulated if it does not allow the exchange of matter with the outside. It does not allow heat exchange with the external environment.

One example is the universe. Most astronomers also regard the universe as an isolated system. It doesn't allow matter or energy to enter or leave.

3.   Description of a thermodynamic system

At our scale, any physical system can be considered as a thermodynamic system, but hereafter we only consider systems containing too many particles for individual descriptions to be possible.

State of a thermodynamic system

The aim of thermodynamics is to describe, from a macroscopic point of view, i.e. on our own scale, the state of a system based on a small number of parameters (temperature, pressure, electrical charge,etc.). Some of these parameters, such as volume or mass, are proportional to the quantity of matter; they are extensible variables. Others, such as temperature or pressure, are independent of the quantity of matter present, and are therefore called intensive. In general, these variables are not independent.

State variables (parameters or quantities)

A state variable is a macroscopic quantity that defines the state of a system at equilibrium. A state variable is measurable and is characteristic of a system state.

Status functions

A state function (X) is an extensive quantity thatdepends only on the state variables. It is constant for a given state of the system. Its variation depends only on the initial and final states of the system, and is independent of the transformations that take the system from one state to the other: $\Delta X = X_{final} - X_{initial}$.

Example:

The height variable **H** is a state function

Work **W** is not a state function

U: internal energy is a state function $\int_{1}^{2} dU = \Delta U$

Heat **Q** is not a state function

Extensive and intensive quantities

- *Extensive variables:* proportional to the overall quantity of matter in the system (e.g.mass m, volume V, length l).

- *Intensive variables:* are independent of the overall quantity of matter in the system (examples: pressure P, temperature T, density ρ).

Equation of state for perfect gases :

are relationships linking several state variables to each other, enabling a system to be describedcompletely without knowing all the variables. For example, the equation of state for a perfect gas is :

$PV = nRT$ .... (*I.19*)

Example:

The equation of state expresses one state variable as a function of the other two,

for perfect gases :

- In terms of pressure: $P = nRT/V$ /

- In terms of volume: $V = nRT/P$ /

- In temperature terms: $T = PV/nR$ |

- In terms of mass: $m = MPV/RT$ |

- In terms of the universal perfect gas constant : $R = PV/mr$ |

- In terms of density: $\rho = m/V = MP/RT$

Equation of state for real gases (Vander Waals, Berthelot,)

The Van Der Waals model takes into account repulsive interactions between particles at very short distances and attractive interactions between particles at long distances. The equation of state for 'n' moles of gas is of the form :

$$P = \frac{nRT}{V - nb} + \frac{a.n^2}{V^2} \qquad\qquad (I.20)$$

With :

a: cohesion term (constant).   *b* : molar covolume (constant).

 n: number of moles.   *P*: pressure.

R: perfect gas constant.   *T*: absolute temperature.

V: volume.

4. Evolution and thermodynamic equilibrium states of a system

A system is in a state of equilibrium when all its defining variables are constant. In other words, there is nospontaneous evolution of the system.

Mechanical equilibrium

The state of mechanical equilibrium of a system is given by the minimum potential energy. Similarly, in thermodynamics, the state of equilibrium corresponds to the minimum of a thermodynamic potential, this potential being determined by the constraints imposed on the system.

Thermal equilibrium state

Thermal equilibrium is achieved when a body with a higher temperature transfers thermal energy to another body with a lower temperature.

Chemical equilibrium

A chemical equilibrium is the result of two simultaneous chemical reactions whose effects cancel each other out.

Example:

A reaction such as the combustion of propane with oxygen, which stops when one of the reactants is completely exhausted, is referred to as a total, complete or irreversible reaction.

5. Possible transfers between the system and the external environment

A distinction is made according to the possibility of transferring matter and/or energy between the systemand the external environment:

- Closed system: no transfer of matter with the outside environment (through surface S). Only energy exchanges are possible.

- Open system: matter and energy can be transferred to the outside environment.

- Isolated system: no transfer (material or energy) possible with the external environment.

> ### *Example:*
>
> - Isolated system: the universe, water in a closed plastic bottle.
>
> - Open systems: living beings, water boiling in a pan, wood burning.
>
> - An open system: thermos flask

Energy transfers or exchanges (work, heat)

An energy transfer is the movement of energy from one place to another without changing the form of energy involved. During an exchange with the external environment, the system can either give or receive energy.
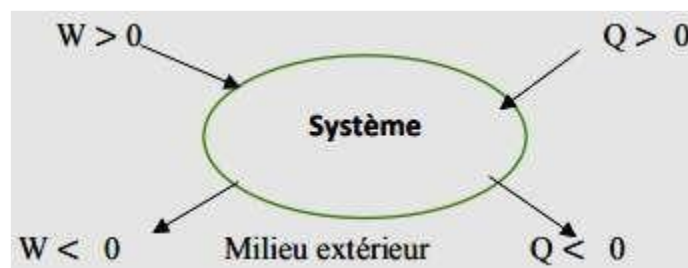

Fig.I.2: Exchange of energy with the external environment [2].

By convention, we have:

- $Q > 0$: heat enters the system (endothermic process)

- $Q < 0$: the system gives up heat to the outside environment (exothermic process).

- $W > 0$: the system receives work (receiving system).

- $W < 0$: the system supplies work (motor system).

Unit: [W]: Joule; [Q]: Joule or calorie; where: 1 calorie = 4.18 joules.

Material transfers or exchanges

During an exchange with the external environment, the
system can transferto the outside world.

System	Material exchange	Energy exchange
Isolated	No	No
Closed	No	Yes
Open	Yes	Yes

6. Transformations of the state of a system (operation, evolution)

A transformation of a system from an initial equilibrium state 1 to a final equilibrium state 2
is accompanied by changes in one or more state variables, or an exchange of energy in the
form of heat *Q* and work *W* with the external environment.

Transformations of a perfect gas :

There are several transformations for a perfect gas, they are defined as follows:

Isochoric transformation of a perfect gas :

Is a transformation that takes place at constant volume *V2 = V1* (final volume v_2 is equal to
initial volume v_1); in this transformation the work of the pressure forces exchanged between
the system and the external medium is zero (*W = 0*).

$$W_{1\to2} = -\int_1^2 PdV = 0 \dots\dots\dots\dots\dots\dots\dots\dots\dots (I.21)$$

Isobaric transformation of a perfect gas :

Transformation taking place at constant pressure *P1 = P2* (pressure of final state *P2* is equal to
the initial pressure *P1*).

$$W_{1\to2} = -P\int_1^2 dV = -P(V_2 - V_1) \dots\dots\dots\dots\dots\dots\dots\dots (I.22)$$

Isothermal transformation of a perfect gas :

Transformation t a k i n g place at constant temperature *T2=T1* (Temperature ofThe final state
T2 is equal to the initial temperature *T1*).

$$W_{1 \rightarrow 2} = -\int_1^2 PdV = -\int_1^2 -nRT \frac{dV}{V} = nRT \ln\frac{V_1}{V_2} = nRT \ln\frac{P_2}{P_1} \cdots\cdots\cdots (I.23)$$
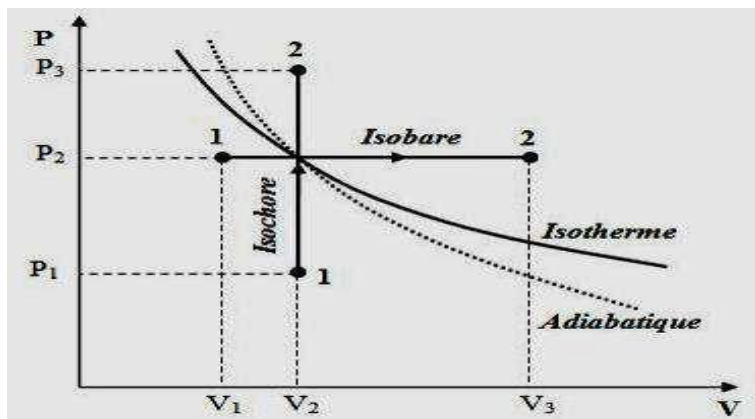

Fig.I.3: *The main thermodynamic transformations* **[3,6].**

Adiabatic transformations of a perfect gas :

Is a transformation that takes place without heat exchange with the external environment (*Q = 0*).

Transformations (open, closed or cyclic):

Is a transformation characterized by the same values of state variables, i.e. the final state is identical to theinitial state *T2 = T1 , P2 = P1 , V2 = V1* (series of successive transformations with a return to the initial state).

Monothermal transformations :

Is a process that takes place in a system at a constant external temperature. The system temperature mayvary, or even not be defined, if the system is not in thermal equilibrium.

Infinitesimal transformations:

A transformation is **infinitesimal** when the initial and final equilibrium states are **infinitely close**.

$$dQ = m.c.dT \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (I.24)$$

Quasi-static transformations :

the transformation is sufficiently slow for the system to go from a continuous sequence of equilibrium statesinfinitely close to *i* to *f*.
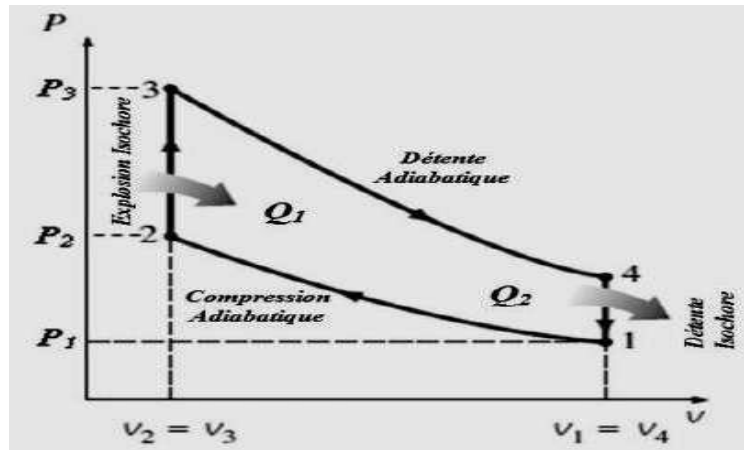
Fig.I.4: *Example of a thermodynamic cycle* **[6].**

Reversible and irreversible transformations :

A transformation is said to be reversible if it verifies both conditions:

- It must be infinitely slow.

- It must be reversible, i.e. it must go through the same states again. balance in the opposite direction **B→A** than in the direct direction **A→B**.

A real transformation is irreversible, either because it is rapid (brutal), or because, although slow, it cannot be reversed.
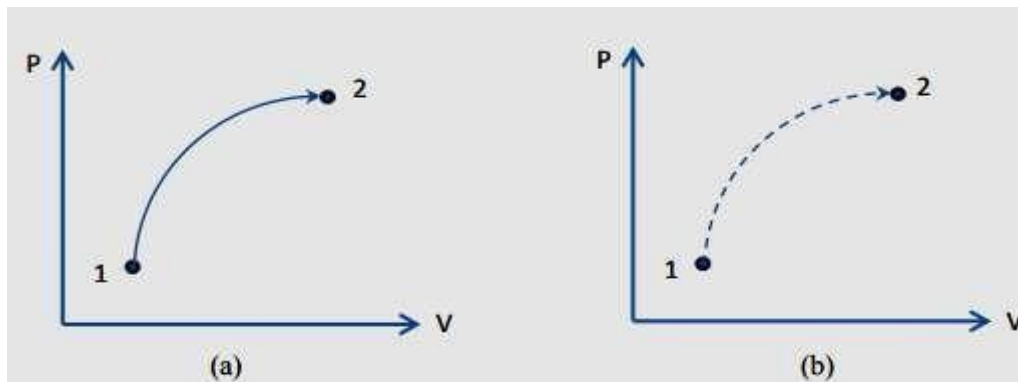

Fig.I.6 : *Transformations: (a) irreversible and (b) reversible* **[7].**

Physical transformations or transformations involving a change of physical state (fusion, vaporization, sublimation, condensation, etc.):

A change of state is a physical transformation during which the physical state of a body changes. Duringa change of state, the various chemical species are preserved (in kind and in quantity), but the chemical entities undergo modifications in their organization: their freedom to move is altered.
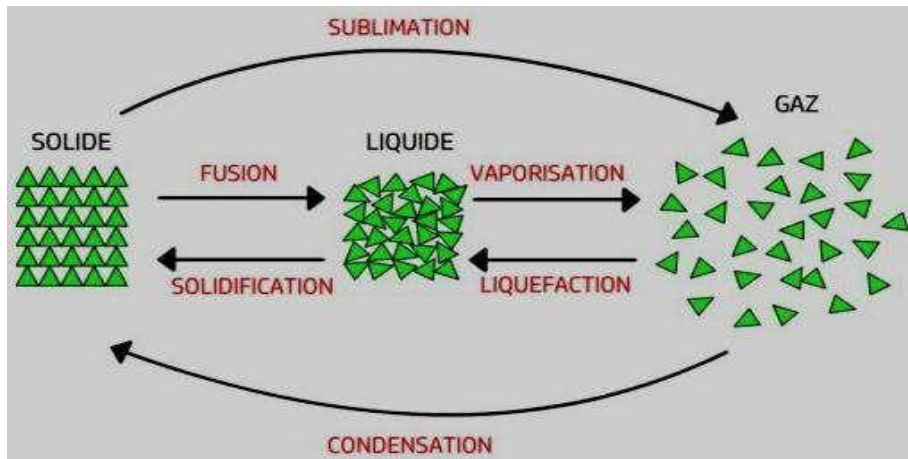
Fig. I.7: Diagram of the main changes of state **[8].**

Chemical transformations or reactions (Combustion, esterification, explosion, corrosion, discoloration...)

A chemical reaction is a transformation of matter during which the chemical species that make up matter are modified: the species that are consumed are called reactants. The species formed during the reaction are called reaction products. A reaction can release energy (usually in the form of heat, but also light), in which case it is an exothermic reaction. It may require energy input, in the form of heat (i.e. "producing cold") or light, in which case it is an endothermic reaction.
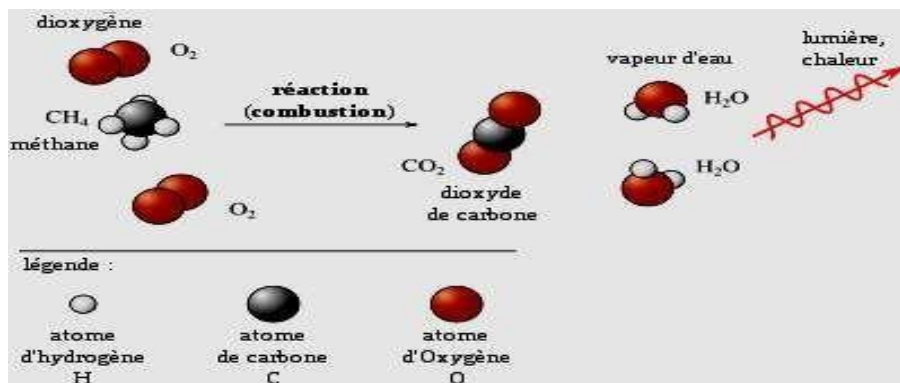

Fig.I.8: Example of methane combustion in oxygen **[9]**.

Graphical representation of perfect gas transformations :

Changes in the state of the system following a transformation are represented byin various diagrams, allowing you to follow the evolution of the system.

Different types of transformation can be distinguished as a result of energy exchange between the system and the external environment. These evolutions are easily represented in these diagrams by vertical or horizontal lines:

- An isochoric transformation (*V = constant*) ;

- An isobaric transformation (*P = constant*);

- An isothermal transformation (*T = constant*) ;

- An isentropic (adiabatic) transformation (*Q = constant*)

I.8.4.1. Clapeyron diagram:P=f(V) in the (P, V) plane

Is a representation where   the pressure P of a thermodynamic system as a function of its mass volume V (in physics), or of molar volume (in chemistry) to follow the evolution of a transformation. It is only possible to draw such a diagram only when the pressure defined in the system, i.e. in a quasi-static transformation.
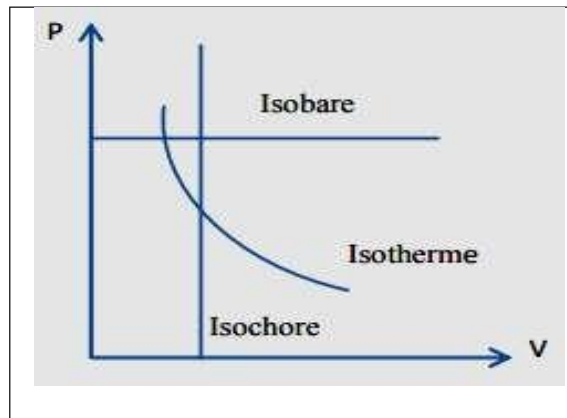

Fig.I.9: Clapeyron diagram [7].

I.8.4.2 Amagat diagram: PV=f(P) in the (P,V) plane

This diagram is named after the French physicist Émile Amagat (1841-1915), who worked in particular on high-pressure gases. is a thermodynamic diagram showing, for a given fluid at constant temperature, the variation of the product of pressure and volume as a function of the pressure applied to the fluid. It can also represent the evolution of the compressibility factor as a function of pressure.
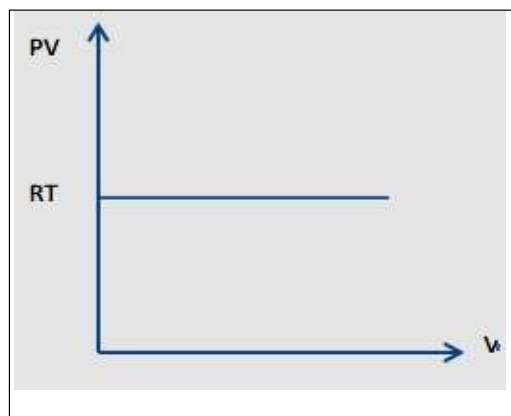

Fig.I.10 : Amagat diagram [7].

7. Reminder of the laws of perfect gases

Un gaz est dit parfait s'il est placé dans les conditions des gaz parfait, qui semanifestent par la basse pression et la température élevée. A basse pression les forces deVan der Walls sont absentes ce qui laisse supposer que la forme des atomes et molécules est sphérique.

8.   Boyle-Mariotte law:pV=Cste at T= Cste

This law shows that the product of the pressure of a gas and its volume depends only on temperature. It is stated as follows:

At constant temperature, the pressure 'P' of a given mass 'm' of gas is inversely proportional to its volume 'V'. P.V = constant.
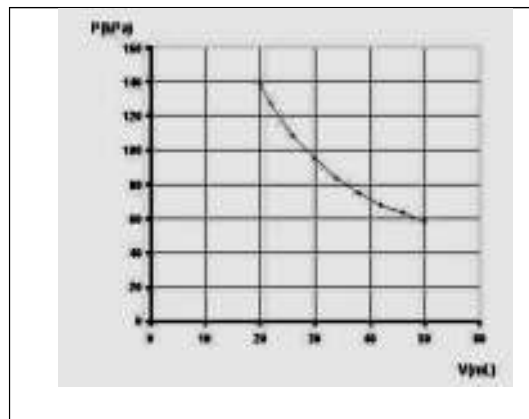
P1V1=P2V2=P3V3=P4V4=Cste

Fig.I.11: Example of Boyle-Mariotte Law [10].

Gay-Lussac's law:V/T=Cste to P=Cste

It states that, at constant volume, the pressure of a quantity of gas is directly proportional to its absolute temperature. **P.V = n.R.T ; V = cst ==> P = cste .**
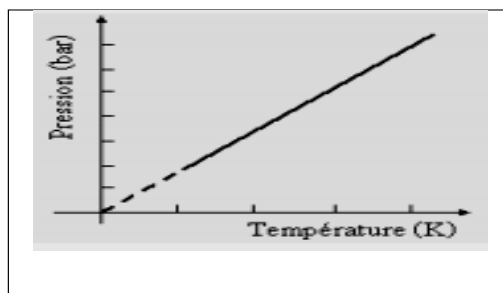
$$T ==> P \propto T. \qquad \frac{V_1}{V_2} = \frac{\overline{T_1}}{T_2}$$

Fig.I.12 : Example of Gay-Lussac's law [10].

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Charles' Law: P/T =Cste at V =Cste

It states that, at constant pressure, the volume occupied by a quantity of gas is directly proportional to its absolute temperature.

P.V = n.R.T ; P = cste ==> V = cste .

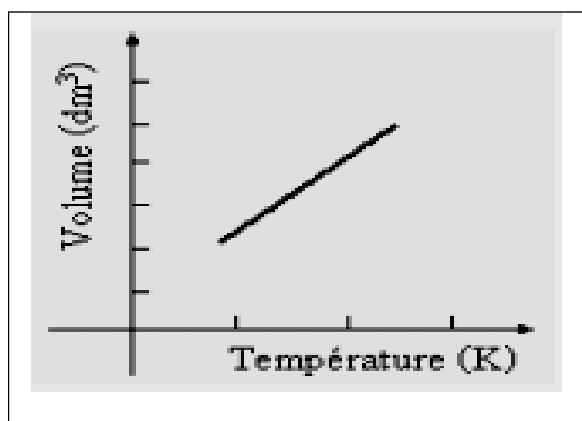$$T ==> V \propto T \Rightarrow \qquad \frac{P_1}{P_2} = \frac{T_1}{T_2}$$

Fig.I.5 : Example of Charles' law [10].

Dalton's law; partial pressures: Pi = xi .PT

In a gas mixture, partial pressure of the gas is the pressure at which is

$$P_{totale} = P_{gaz1} + P_{gaz2} + P_{gaz2} + ... \Rightarrow P_T = \sum P_i \quad .... \quad (I.24)$$

subjected to each gas separately.

Dalton's law using gas mole fraction xi:

$$x_i = \frac{P_i}{P_T} \Rightarrow P_i = x_i.P_{Tot} .... (I.25)$$

$$x_i = \frac{n_i}{n_{Tot}} ....(I.26)$$

With:

$$\sum x_i = 1 \quad .... (I.27)$$

Example:

A mixture of three gases: *O2; N2; CO2 :*

What is the partial pressure of *O2* at *P=1atm* and *T=273.15 K?*

If *(N2)=0.1 mol, (CO2)=0.4 mol, nT=2mol.*

Calculate *P(O2)=?*

Solution:

P (O2)= x (O2) .P

We have: *nT = n(N2) + n(O2) + n (CO2)* $\longrightarrow$ *n (O2) = nT - [n(N2) +*
n (O2)] A.N:n(O2)= 2-(0.1+0.4)=1.5 mol

x(O2)= n(O2) / n

= 1.5 / 2 =0.75

P(O2)= x(O2) .P=0.75atm