Chapter 1: General Concepts in Thermodynamics

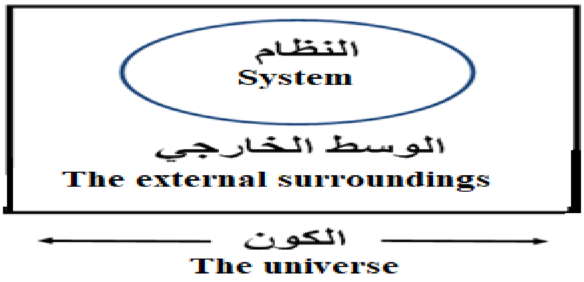
1- Introduction:

Thermodynamics is the science that studies energy exchanges between systems or between a system and its surroundings.

- It does not concern itself with the rate of system reactions (chemical kinetics).
- Nor does it concern itself with the mechanisms governing these transformations. Thermodynamics focuses on:
- The conversion of heat into mechanical work.
- The conversion of energy into mechanical work.

2- System:

It is any part of the universe that we want to subject to study and can be treated as a unit with specific properties.

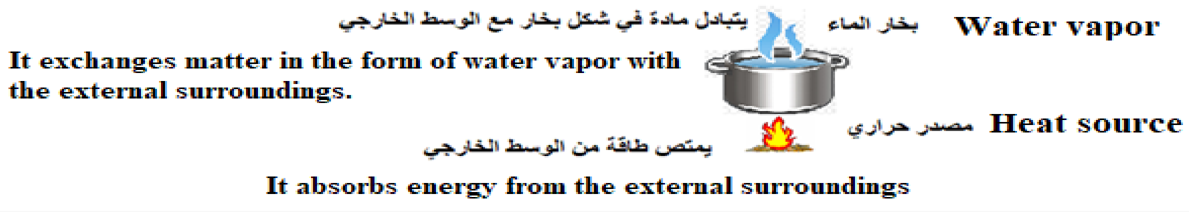


An important aspect of thermodynamics is the mutual interaction between the system and the external surroundings. As a result, there are different types of systems.

2-1- Open System: This is a system that allows for the exchange of both matter and energy with the external surroundings.

Examples:

A cooking pot with boiling water



Electric clothes iron powered with water.

2-2- Closed System: This is a system that allows for the exchange of energy without matter with the external surroundings.

Examples:

- A cup of boiling water, but sealed.
- Electric clothes iron that works only with electricity.

2-3- Isolated System: This is a system that does not allow for the exchange of either energy or matter with the external surroundings.

Example : A calorimeter.

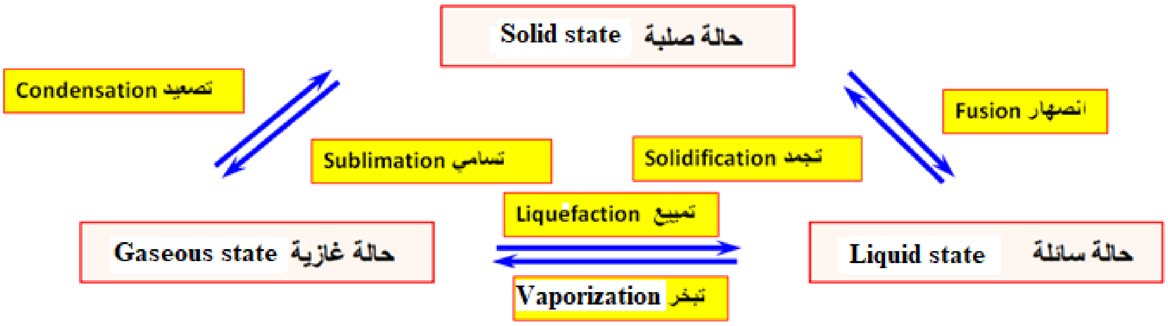
And the following table summarizes the known systems:

Exchange in energy	Exchange in matter	The system
No	No	Isolated
Yes	No	Closed
Yes	Yes	Open

3- System State: The state of a system is defined by several variables (physical quantities) such as mass (m), pressure (P), temperature (T), volume (V), number of moles (n), and others. These are called state variables or state functions, and they are known and constant values that enter into the description of the system's state.
Under the influence of energy exchange or transfer between the system and the external surroundings, the system evolves from state (1) to state (2).

$$\begin{tikzcd} \text{The state (1)} \arrow[r] & \text{The state (2)} \\ P_1, V_1, T_1 & P_2, V_2, T_2 \end{tikzcd}$$

4- Physical Transformations of Matter:



5- Phases of Matter: A phase is each homogeneous part that makes up a substance or system.

Examples:

•A mixture of gases (H_2, O_2, N_2…) → Homogeneous mixture → the number of phases is 1.

- A liquid mixture → Homogeneous mixture like water +alcohol → Monophasic
  → Heterogeneous mixture like water+ oil → two phases
- A solid mixture: the number of phases is the same of the constituent materials except in the case of the formation of a single crystal from the total of the reactive materials.

$$Fe + C \rightarrow FeC$$

6-Variables and State Functions: Variables are the physical quantities that enter into the description of the system's state.

6-1- Extensive Variables: These are all the variables that are proportional to the quantity of matter for a homogeneous system, such as mass, volume, length, energy…………, and they are cumulative.

Example: Variables m (mass) and V (volume)

When two systems of the same nature are combined, the mass and volume of the new system are respectively the sum of the masses and volumes of the two original systems.

$$\boxed{m_1 , V_1} + \boxed{m_2 , V_2} \longrightarrow \boxed{m_1 + m_2 , V_1 + V_2}$$

So, volume and mass are extensive variables.

6-2- Intensive Variables: Intensive (implicit) variables: These are those properties that are independent of the amount of matter or materials contained in the system, or they are properties that are not proportional to the amount of matter, and they are not cumulative when two systems are combined or combined, such as: temperature, pressure, volumetric mass.

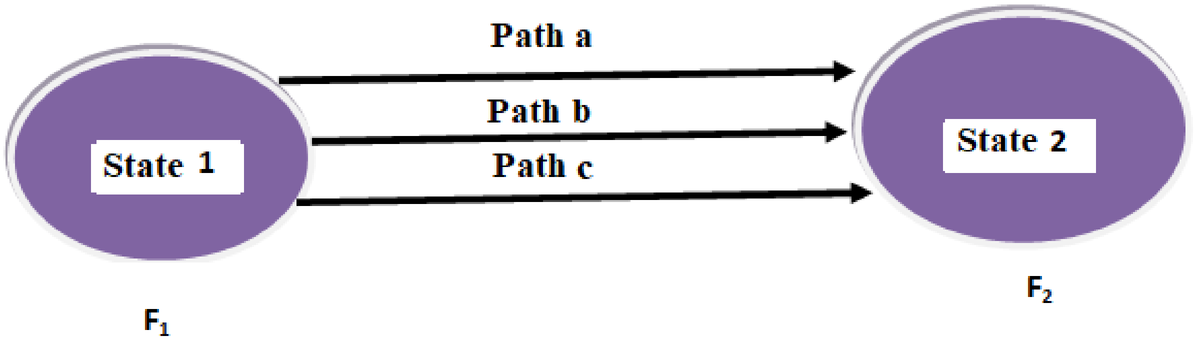
For example:

- The volumetric mass of benzene is the same whether it's 1 mole or 10 moles.
- The concentration of salt in seawater is the same whether in a drop or 1 liter.
- When mixing water at a temperature of 20°C with water at a temperature of 50°C, we don't obtain water at a temperature of 70°C.

And we can summarize some of the variables in the following table:

Intensive variables (المتغيرات الضمنية)	**Extensive variables (المتغيرات الممتدة)**
• Pressure P	• Length L
• Temperature T	• Volume V
• Density d	• Area S
• Volumetric mass ρ	• Mass m

6-3- The state function: It is a mathematical function defined to describe the state of a system, and its value is independent of the specific path taken to transition from state A to state B.
In other words, the function concerns itself with the initial and final states of the system, and mathematically, this means that the partial derivatives of the function with respect to its variables are equal.



If F is a state function $\Longrightarrow \Delta F = F_2 - F_1$ whatever the path taken for the transformation a, b, c.

For example: the work is not a state function $\Longrightarrow w = F_{\text{القوة}} \times L_{\text{الانتقال}}$ so, work is related to the path followed.

$$\int_1^2 \delta w = w \neq \Delta w$$

Exemple:

f(x,y) = $x^2y + y^3$ Prove that f is a state function

$$df(x,y) = \left(\frac{\sigma f}{\sigma x}\right)_y dx + \left(\frac{\sigma f}{\sigma y}\right)_x dy = (2xy)\,dx + (x^2 + 3y^2)dy$$

Calculs of Variations:

$$\left[\frac{\sigma\left(\frac{\sigma f}{\sigma x}\right)_y}{\sigma y}\right]_x = 2x = \frac{\sigma^2 f}{\sigma y \sigma x}$$

$$\left[\frac{\sigma\left(\frac{\sigma f}{\sigma y}\right)_x}{\sigma x}\right]_y = 2x = \frac{\sigma^2 f}{\sigma x \sigma y}$$

Therefore, the partial derivatives are equal to each other, and thus the differential equation is exact $\Longrightarrow$ f(x, y) is a state function.

Let's take another example: f(x, y) = $xy^2 + y^3$

To prove that this function is a state function, we need to show that its partial derivatives are equal, which implies that it's an exact differential.

First, calculate the partial derivative of f with respect to x:

$$\left(\frac{\sigma f}{\sigma x}\right)_y = y^2$$

Next, calculate the partial derivative of f with respect to y:

$$\left(\frac{\sigma f}{\sigma y}\right)_x = (2xy + 3y^2)$$

Now, we need to check if these partial derivatives are equal:

$$\left[\frac{\sigma\left(\frac{\sigma f}{\sigma x}\right)_y}{\sigma y}\right]_x = 2y = \frac{\sigma^2 f}{\sigma y \sigma x}$$

$$\left[\frac{\sigma\left(\frac{\sigma f}{\sigma y}\right)_x}{\sigma x}\right]_y = 2y = \frac{\sigma^2 f}{\sigma x \sigma y}$$

Since $\frac{\sigma^2 f}{\sigma y \sigma x} = \frac{\sigma^2 f}{\sigma x \sigma y}$, the partial derivatives are equal.

Therefore, $f(x, y) = xy^2 + y^3$ is a state function, and its differential equation is exact.

7- The Ideal gas equation:

7-1- Ideal gas: it is any gas in which there are no interactive forces between its components (molecules). The conditions that must be met for a gas to be considered ideal or perfect are as follows:

- The volume of its molecules is negligible compared to the container it occupies (under low pressure).
- Collisions between gas molecules are elastic, and intermolecular forces are negligible.
- Gas molecules move randomly without external influences."

7-2- Gas Variables :

- Pressure P
- Temperature T
- Volume V
- Amount of substance (mass or number of moles) $n = \frac{m\ (mass)}{M\ (Molar\ mass)}$

And there is a set of laws that distinguish ideal gases, including:

7-2-1- The Relationship between Pressure and Volume (Boyle's Law): At a constant temperature, the product of PV for the same amount of gas remains constant

$$P_1V_1 = P_1V_1 = \cdots \ldots \ldots Cst$$

Example: A sample of gas has a volume of 75 L at a pressure of 5 atm and a temperature of 0°C. We compress it while keeping the temperature constant until its volume becomes 30 L. What is the final pressure of the gas?

Solution :

$$T\ Cst \Rightarrow P_1V_1 = P_2V_2 \Rightarrow P_2 = \frac{P_1V_1}{V_2} = \frac{5 \times 75}{30} = 12.5\ atm$$

7-2-2- The relationship between pressure and temperature (Gay-Lussac's Law): When the volume of gas and the amount of substance are held constant, and we change the temperature, the ratio of pressure to its absolute temperature remains constant, whether in the case of cooling or heating.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{P}{T} = constant$$

(When volume and the quantity of substance are held constant)

Example: A container with a volume of 10L is filled with gas at a pressure of 2 atm and a temperature of 0°C. If we heat this gas while keeping its volume constant, what is the temperature at which the gas pressure becomes equal to 2.5 atm?

Solution :

$$V = Cst \Rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow T_2 = \frac{P_2 \times T_1}{P_1} = \frac{2,5 \times 273}{2} = 341\ K$$

7-2-3- The relationship between volume and temperature (Charles's Law): When the pressure of a gas and the quantity of its substance are held constant, the ratio of its volume to its absolute temperature remains constant, whether in the case of heating or cooling, i.e.,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V}{T} = constant$$

(When pressure and the quantity of substance are held constant)

7-2-4- The relationship between pressure and quantity of substance (P = f(n)): We keep the volume and temperature constant and change the number of moles of the gas each time, and we read the pressure value each time.

$$\frac{P_1}{n_1} = \frac{P_2}{n_2} = \frac{P}{n} = constant$$

The general law of ideal gases

From the previous relationships, we find:

$$\left[\begin{array}{l} P.V = Cst \\ \frac{P}{T} = Cst \\ \frac{V}{T} = Cst \\ \frac{P}{n} = Cst \end{array}\right.$$

Which means that P is inversely proportional to V and inversely proportional to T and n

⇩

$$P = \frac{Cst\,.\,T\,.\,n}{V} \Rightarrow P = \frac{R.\,T.\,n}{V} \Rightarrow PV = RTn$$

$$R = \textbf{Ideal Gas Constant} = Cst$$

In experiments, it has been observed that ideal gases exhibit the following:

- 1 mole of these gases under standard conditions of pressure and temperature (0°C, 1 atm) occupies a volume of 22.4 L.
- 1 mole of these gases contains 6.023×10^{23} molecules, and this number is known as **Avogadro's number**.

Therefore :

$$PV = nRT \Rightarrow R = \frac{PV}{nT} \text{ (The Equation of State for Ideal Gases)}$$

The unit and value of the universal gas constant R: When specifying the value of R, it is important to choose the appropriate units for the constant, as they play a significant role when used in physical calculations. Its general unit is : energy unit × Kelvin^{-1} × mole^{-1}.

Whereas :

$$R = \frac{PV \leftarrow \ energy}{nT}$$

$$(Pressure)\ P = \frac{F(Force)}{S\ (surface)} = N.m^{-2} = Pa\ (IS)$$

$$(Volume) V = \ m^3\ (IS)$$

$$P.V = N.m^{-2}.m^3 = N.m = Force \times Transition = W\ (work) = energy\ (J)$$

$$J(IS) = N.m = Pa.m^3$$

<u>Pressure units :</u>

$$1\ atm\ = 1,01325\ bar\ = 1,01325.10^5\ Pa$$

$$1\ atm\ = 760\ mmHg\ = 760\ Torr$$

<u>In terms of volume :</u>

$$1\ L = \ 10^{-3}\ m^3$$

Regarding temperature, in the laws of thermodynamics, T (K).

So :

$$R = \frac{energy}{mol \times temperature} = energy \times K^{-1} \times mol^{-1}$$

energy is measured in various units, which can be: atm·L; cal; erg; J.

$$1\ atm\ .L = 1,01325.10^2\ \underbrace{Pa.m^3}_{J} = 1,01325.10^2\ J = 24\ ,24\ cal$$

<u>Whereas :</u>

1 cal = 4,18 J

1J = 10^7 erg

<u>And thus, the constant R takes the following values:</u>

$$R\ = 8,314\ J.K^{-1}.mol^{-1}$$

$$R = 8,314\ Pa.m^3.K^{-1}.mol^{-1}$$

$$R = 0,082\ atm.L.K^{-1}.mol^{-1}$$

$$R = 1,987 \approx 2\ cal.K^{-1}.mol^{-1}$$

8- The Law of Partial Pressures (Dalton's Law):

Let there be a mixture consisting of several gases inside a container with a volume V, at a temperature T, and subjected to a total pressure P_T. We represent by the symbol ni the number of moles of gas i. The partial pressure of component i is defined as the pressure exerted by this gas on the walls of the container as if it occupied it alone, and it is symbolized by Pi.

We have:

The total of these gases exhibits ideal gas behavior

$$\left[\begin{array}{l} P_T V = n_T RT \\ P_i V = n_i RT \end{array}\right.$$

V : Vessel volume

P_T : Total pressure of the gas mixture

n_T : Total moles (sum of gases) $= \Sigma n_i$

By dividing, we find :

$$\frac{P_T}{P_i} = \frac{n_T}{n_i} \Rightarrow P_i = \frac{n_i}{n_T} . P_T$$

$$\frac{n_i}{n_T} = \frac{\text{Number of moles of the gas } i}{\text{Total moles } = \Sigma n_i} = x_i \text{ (Mole fraction)}$$

Whereas : $\Sigma x_i = 1$ و $0 \leq x_i \leq 1$

Therefore ;

$$P_i = x_i . P_T \text{ Dalton's Law}$$

$$P_T = \frac{n_T}{V} RT = \frac{(n_1 + n_2 + \cdots \ldots\ldots)}{V} RT = \frac{n_1}{V} RT + \frac{n_2}{V} RT \ldots\ldots = P_1 + P_2 + \cdots ..$$

$$= P_T$$

$$P_T = \sum P_i$$

The total pressure of the gas mixture equals the sum of the partial pressures.

To calculate the partial pressure of a gas from this mixture, we isolate each gas in a container with the same total volume V and at the same temperature T.

Example: Consider a gas mixture composed of:

0.15 g of H_2

0.7 g of N_2

0.34 g of NH_3

Under a total pressure of 1 atm and a temperature of 27 °C.

- Calculate the molar fraction for each gas.
- Calculate the partial pressure for each gas.

The Solution:

$$x_i = \frac{n_i}{n_T} \;;\; n_T = n_{H_2} + n_{N_2} + n_{NH_3}$$

$$n_{H_2} = \frac{m_{H_2}}{M_{H_2}} = \frac{0,15}{2} = 0,075\ mol$$

$$n_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{0,7}{28} = 0,025\ mol$$

$$n_{NH_3} = \frac{m_{NH_3}}{M_{NH_3}} = \frac{0,34}{17} = 0,02\ mol$$

$$n_T = 0,075 + 0,025 + 0,02 = 0,12\ mol$$

$$x_{H_2} = \frac{n_{H_2}}{n_T} = \frac{0,075}{0,12} = 0,625$$

$$x_{N_2} = \frac{n_{N_2}}{n_T} = \frac{0,025}{0,12} = 0,208$$

$$x_{NH_3} = \frac{n_{NH_3}}{n_T} = \frac{0,02}{0,12} = 0,167$$

Calculating the partial pressures :

$$\mathrm{P_i} = x_i\,.\,P_\mathrm{T}$$

$$\mathrm{P}_{H_2} = x_{H_2}\,.\,P_\mathrm{T} = 0,625.1 = 0,625\ atm$$

$$\mathrm{P}_{N_2} = x_{N_2}\,.\,P_\mathrm{T} = 0,208.1 = 0,208\ atm$$

$$\mathrm{P}_{NH_3} = x_{NH_3}\,.\,P_\mathrm{T} = 0,167.1 = 0,167\ atm$$