Introduction

The word "thermodynamics" is composed of two parts: "thermo," which means heat, and "dynamics," which signifies work or movement. The compound word 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.
Thermodynamics has several branches:

- **Classical Thermodynamics:** considers systems in their macroscopic aspects using measurable quantities such as pressure P, temperature T, and volume V).

- **Chemical Thermodynamics:** studies the heats of reactions and the thermodynamic properties of chemical equilibria).

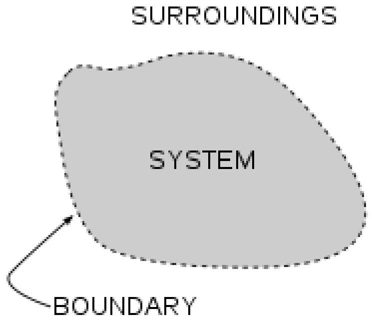
- **Statistical Thermodynamics:** takes into account systems in all their aspects microscopic aspects and is based on statistical mechanics.

- **Technical Thermodynamics:** applies thermodynamics to studying thermal machines, refrigeration systems, etc.

1.1. Definition of Thermodynamic Systems and the External Environment:

1.1.1. Definition of a System:

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



Universe = system + external environment (surrondings).

1.1.2. Types of systems:

Based on the nature of the boundary between the system and the external environment, different types of systems can be distinguished:

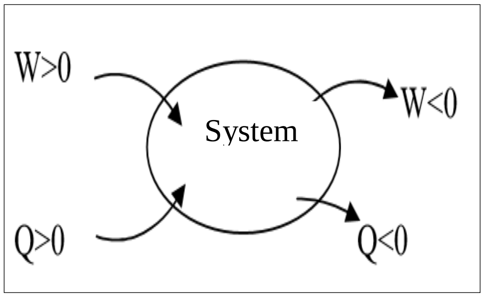
a) Open System: Can exchange both energy and matter with the external environment.
Example: water boiling in a pan, wood burning.

b) Closed System: Can exchange energy but not matter with the external environment.
Example: a closed water bottle

c) Isolated System: Cannot exchange either energy or matter with the external environment.
Example: the universe

1.1.3. Sign Convention:

W: Amount of work exchanged between the system S and the external environment.
Q: Amount of heat exchanged between the system S and the external environment.



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).

W and Q are considered positive (+) when they are received by the system and negative (-) when the system provides them.

1.2. Description of a Thermodynamic System:

1.2.1. State Parameters: State Variables.

The state of a system is described by a set of macroscopic variables known as "state variables." State variables characterizing a physico-chemical system include temperature, pressure, volume, mass, concentration, density, number of moles, partial pressure, and more. State variables can be either extensive or intensive:

a) Extensive Variable: A variable that is proportional to the quantity of matter and is an additive quantity. Examples include mass, volume, and quantity of matter.

b) Intensive Variable: A variable independent of the quantity of matter. Examples include temperature, concentration, and density.

1.2.2. State Function:

A state function (X) is an extensive quantity that depends 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: $\Delta X = X_{final} - X_{initial}$

Mathematical Properties of State Functions:

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

$dF = (\partial F/\partial x)_y\, dx + (\partial F/\partial y)_x\, dy = A\, dx + B\, dy$

$(\partial F/\partial x)_y$: is the derivative of F with respect to x for constant y.

$(\partial F/\partial y)_x$: is the derivative of F with respect to y for constant x.

If $\frac{\partial^2 F}{\partial x\, \partial y} = \frac{\partial^2 F}{\partial y\, \partial x}$ dF is an exact total differential (ETD), then F is a state function.

Example:

$$\mathbf{dF = x^2 y dx + x^3/3\, dy}$$

$$\left(\frac{\partial F}{\partial x}\right)_y = \mathbf{x^2 y}\ ;\ \frac{\partial^2 F}{\partial y\, \partial x} = \mathbf{x^2}$$

$$\left(\frac{\partial F}{\partial y}\right)_y = \mathbf{x^3/3}\ ;\ \frac{\partial^2 F}{\partial x\, \partial y} = \mathbf{x^2}$$

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

Thus, dF is an ETD.

1.3. Equation of State

It is an equation which provides a mathematical relationship between two or more state functions associated with matter such as its temperature, pressure, volume, or internal energy.

1.3. Equation of state for ideal gases:

1.3.1. Ideal gas

An ideal gas is a theoretical concept in thermodynamics that describes a gas with certain idealized properties. These properties include negligible intermolecular interactions, perfectly elastic collisions between molecules.

1.3. 2. Equation of state for ideal gases:

Are relationships linking several state variables to each other, enabling a system to be described completely without knowing all the variables. The equation of state for a ideal gas is:

$PV = nRT$

Where **P** is the pressure, **V** is the volume; **R** is the molar gas constant (**R**=8.314 J/K.mol), **T** is temperature in Kelvin, and **n** is the number of mole of gas.

Note:

Normal temperature and pressure conditions (NTP):

$P = 1$ atm = 1.01325 bar = 1.01325×10^5 Pa = 760 mmHg = 760 Torr.
$T = 0°C = 273.15$ K

The ideal gas equation $PV = nRT$ encompasses the three laws that perfect gases obey:

a) *Boyle-Mariotte law*

At constant temperature (T), the volume (V) of a gas is inversely proportional to its pressure (P).

PV = constant, $P_1V_1 = P_2V_2$ (law of isothermal compressibility).

b) Gay-Lussac's Law:

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

V/T = constant, $V_1/T_1 = V_2/T_2$ (law of isobaric expansion).

c) Charles's Law:

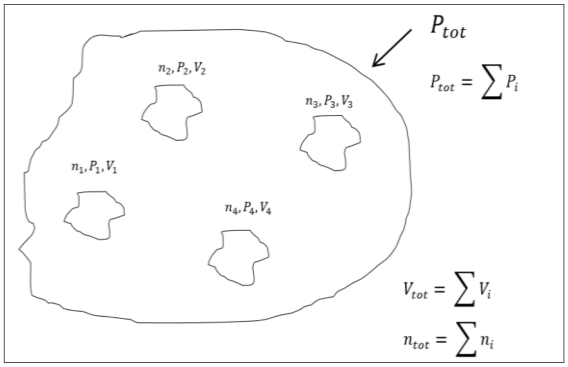
At constant volume (V), the pressure (P) of a gas is proportional to its temperature (T).

P/T = constant, $P_1/T_1 = P_2/T_2$.

1.3.3. Dalton's Law (Mixture of ideal Gases):

Dalton’s law of partial pressure was given by English Chemist, Physicist and meteorologist John Dalton in 1802. According to Dalton’s law of partial pressure, total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual gases in the mixture.

$$P_{tot} = P_1 + P_2 + P_3 + \ldots = \sum P_i$$



By applying the ideal gas law to gaseous species, we have:

$P_i V_{tot} = n_i RT$;

$P_{tot} . V_{tot} = n_{tot} . R . T$

$Pi = x_i P_{tot}$ x_i: molar fraction

1.4. Thermodynamic Equilibrium:

A system is said to be in equilibrium when its properties do not change appreciably with time over the interval of interest (i.e. observation time).

A thermodynamic system is said to be in thermodynamic equilibrium if it is in chemical equilibrium, mechanical equilibrium and thermal equilibrium and the relevant parameters cease to vary with time.

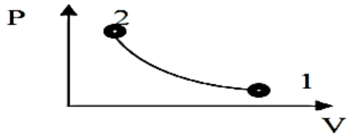
- When the temperature is the same throughout the entire system, we consider the system to be in **thermal equilibrium**.
- When there is no change in pressure at any point of the system, we consider the system to be in **mechanical equilibrium**.
- When the chemical composition of a system does not vary with time, we consider the system to be in **chemical equilibrium**.

1.5. Transformations of the state of a system (operation, evolution) (Thermodynamic Processes)

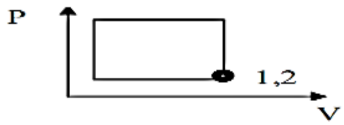
A system undergoes a thermodynamic process when there is some energetic change within the system that is associated with changes in pressure, volume, internal energy, temperature, or any sort of heat transfer.

There are four types of thermodynamic processes that have their unique properties, and they are:

- **Adiabatic Process**: A process where no heats transfer into or out of the system occurs.
- **Isochoric Process:** A process where no change in volume occurs and the system does no work.
- **Isobaric Process**: A process in which no change in pressure occurs.
- **Isothermal Process**: A process in which no change in temperature occurs.
- **Open transformations**: An open transformation is a transformation where the final state of the system is different from the initial state.



- **Cyclic Processes:** These are series of processes in which after certain interchanges of heat and work, the system is restored to its initial state.

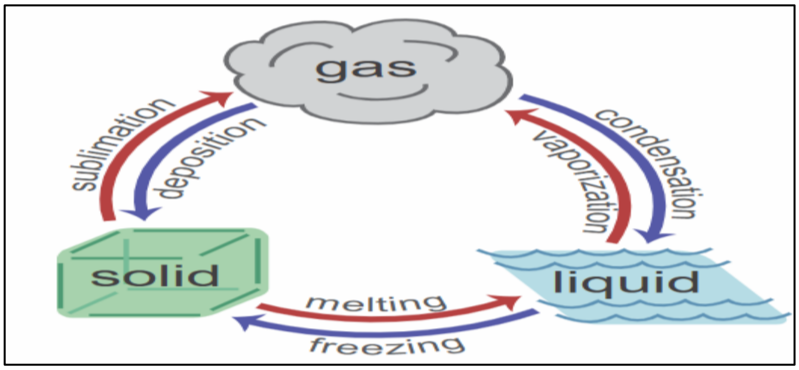


- **Reversible Process**: A reversible process can be defined as one which direction can be reversed by an infinitesimal change in some properties of the system.

- **Irreversible Process**: An irreversible process can be defined as one which direction cannot be reversed by an infinitesimal change in some properties of the system.
- **Quasi-static Process**: This is a process that is carried out in such a way that at every instant, the system departs only infinitesimal from an equilibrium state (i.e. almost static). Thus a quasi-static process closely approximates a succession of equilibrium states.

1.6. 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. During a 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.

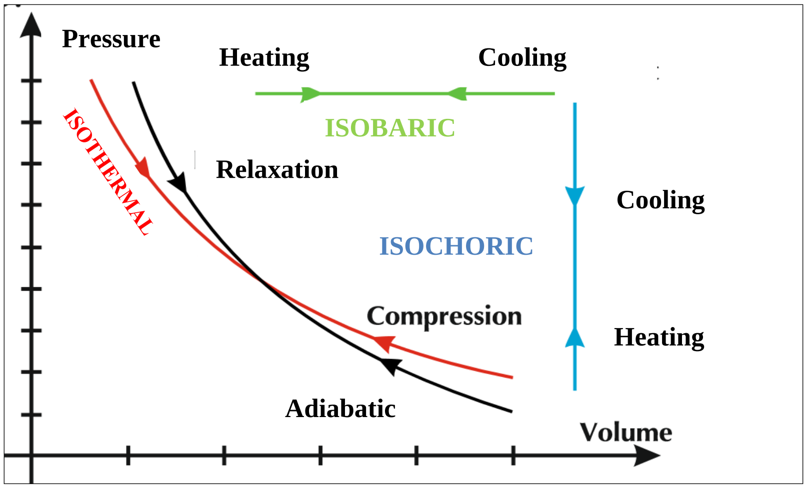


1.7. Chemical transformations or reactions (Combustion, esterification, explosion, corrosion, discoloration...)

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.

1.8. Graphical representation of perfect gas transformations :

This is a simple graphical representation of pressure as a function of volume, P = f(V).



1.9. Temperature:

1.9.1. Concept of Temperature:

Temperature (**T**) is defines as the degree of hotness or coldness of a body.

1.9.2. Temperature Scales :

Available temperature scales are; the Celsius scale (also known as the Centigrade scale), the Fahrenheit scale, the Kelvin scale, the Rankine scale.

Linear Scale: This is the centigrade scale, also known as Celsius, denoted as °C, with reference points at 0 and 100 corresponding, respectively, to the melting and boiling points of water at atmospheric pressure.

Fahrenheit Scale: Denoted as °F, on this scale, the melting and boiling points of water at atmospheric pressure are 32°F and 212°F, respectively. The expression gives the relationship between the Celsius and Fahrenheit scales:

$$T\,(°F) = 32 + 1.8\,T\,(°C).$$

Kelvin Scale: This is the universal scale, also known as the absolute degree, denoted as K, and is the "SI unit of temperature." The relation gives the relationship between the Kelvin and Celsius scales:

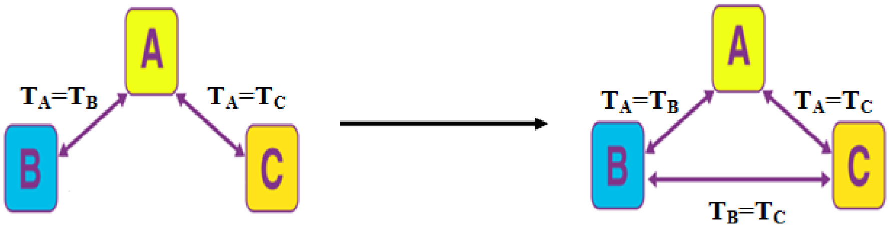
$$T\,(K) = T\,(°C) + 273.15.$$

Rankine Scale (R): An absolute scale used in Anglo-Saxon countries.

$$T(R) = T\,(°F) + 459.67$$

1.10. The Zeroth Law of Thermodynamics:

"When two systems or bodies are in thermal equilibrium with a third system, they are in thermal equilibrium with each other."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