Basics of Thermodynamics

Introduction

Thermodynamics is a branch of physics that studies macroscopic systems (i.e. composed of a large number of particles) using an energetic approach. It is a theory that applies to many systems and allows to establish general relations between the coefficients that describe the various states of matter.

Basic concepts in thermodynamics

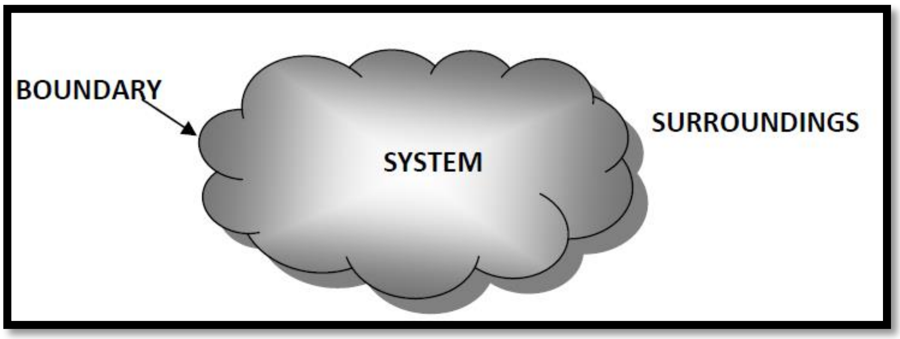
System and environment

Thermodynamics studies a macroscopic system that can be in contact with other macroscopic systems and environment.

A thermodynamic system is the object of the study under review. What is not in the system is defined as the surroundings.

Environment (or **surrounding**, or bath, or heat reservoir) is a special type of a system that has a very large size. The system under consideration can change its state as a result of its contact to the bath but the state of the bath does not change due to the interaction with a much smaller system. For instance, the thermometer measuring the temperature of a body can be considered as the system, whereas the body itself plays the role of the bath.

Boundary: the real or imaginary surface that separates the system from its surroundings. The boundaries of a system can be fixed or movable. Mathematically, the boundary has zero thickness, no mass, and no volume.



Types of systems in thermodynamics

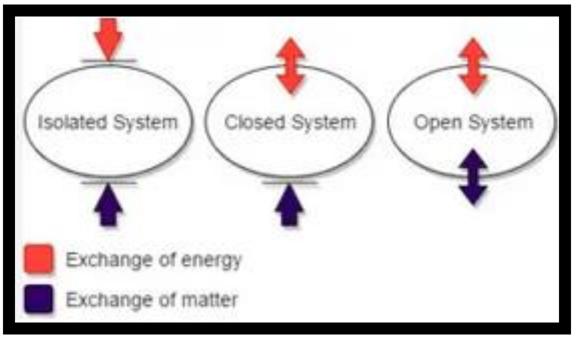
Closed system or **control mass**: consists of a fixed amount of mass, and no mass can cross its boundary. But, energy in the form of heat or work, can cross the boundary, and the volume of a closed system does not have to be fixed.

Open system or **control volume**: is a properly selected region in space. It usually encloses a device that involves mass flow such as a compressor. Both mass and energy can cross the boundary of a control volume.

Isolated system: A closed system that does not communicate with the surroundings by any means.

Rigid system: A closed system that communicates with the surroundings by heat only.

Adiabatic system: A closed or open system that does not exchange energy with the surroundings by heat.



Extensive, intensive, and specific quantities

Macroscopic physical quantities can be **intensive** and **extensive**.

- **Intensive quantities** (pressure P, temperature T) do not depend on the size (mass) of the system,
- **The extensive quantities** (mass M, volume V , energy E or U) scale with the system size.

To make this definition more precise, one can split the system into two equal parts by an imaginary membrane. The intensive quantities of the two resulting systems will remain the same while the extensive quantities of each subsystem will be half of that for the whole system. Specific quantities are the third type of quantities that can be obtained from an extensive quantity by division by another extensive quantity. By this definition, specific quantities do not depend on the system size. An example of specific quantity is the mass density.

Reversible and irreversible processes

We shall find it useful to have in hand definitions for so-called reversible and irreversible processes. Let us take

- **Reversible process**: A process in which it is possible to return both the system and surroundings to their original states.
- **Irreversible process**: A process in which it is impossible to return both the system and surroundings to their original states.

TEMPERATURE

The advantage of the **Celsius** scale is using very natural events, melting of ice and boiling of water (at normal conditions), to define the basic temperature points **0 °C** and **100 °C**.

Physicists use the **Kelvin** scale in which the temperature, corresponding to the extrapolated point, where the volume (or pressure) of the ideal gas vanishes, is set to zero and one degree of temperature difference is the same as in the Celsius scale. The relation between the two scales is **T (°K) = T (°C) +273.15**

Standard temperature and pressure (STP)

T = 0 °C = 273.15 K

P = 1 atm

Standard ambient temperature and pressure (SATP)

T = 25 °C = 298.15 K

P = 1 bar

Dimensions and Units

Any physical quantity can be characterized by dimensions. The arbitrary magnitudes assigned to the dimensions are called units. There are two types of dimensions, primary or fundamental and secondary or derived dimensions.

Primary dimensions are: mass, m; length, L; time, t; temperature, T

Secondary dimensions are the ones that can be derived from primary dimensions such as: velocity (m/s^2), pressure (Pa = kg/m.s^2).

There are two unit systems currently available SI (International System) and USCS (United States Customary System) or English system. We, however, will use SI units exclusively in this course. The **SI** units are based on decimal relationship between units. The prefixes used to express the multiples of the various units are listed in Table below.

MULTIPLE	10^{12}	10^{9}	10^{6}	10^{3}	10^{-2}	10^{-3}	10^{-6}	10^{-9}	10^{-12}
PREFIX	tetra, T	giga, G	mega, M	kilo, k	centi, c	mili, m	micro, µ	nano, n	pico, p

1 Calorie = 4.18 J

1 Joule = 10^7 erg

1 L. atom = 24.23 cal = 101.3 J

1 atm = 1,013 bar = 1,013 10^5 Pa = 76 cmHg = 760 Torr

1 bar = 10^5 Pa

Time : s

Temperature: Kelvin

Pression: Pa [N/m^2]

1 Pa = 1 N/m^2

Energie : Joule

Puissance: Watt ; 1 W = 1 J/s

Ideal gas

The simplest equation of state is that of the ideal gas that is written in the form:

$$P.V = n.R.T$$

Where **n**: is the number of moles of the gas and **R = 8:314 J/(mole.K)** is the universal gas constant.

Equation of state

Boyle-Mariotte Law: The volume (V) of a given mass of gas at a constant temperature is inversely proportional to its pressure (p).

$$T = Cte$$

$$\mathbf{P_1\,V_1 = P_2\,V_2}$$

Gay-Lussac's law:

$$\boldsymbol{P = Cte}$$

$$\mathbf{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$$

Charles's Law

$$\boldsymbol{V = Cte}$$

$$\mathbf{\frac{P_1}{T_1} = \frac{P_2}{T_2}}$$

Dalton’s law

Dalton's law (also called Dalton's law of partial pressures) states that in a mixture of non-reacting gases, the total pressure exerted is equal to the sum of the partial pressures of the individual gases.

$$\mathbf{P_T\,V = n_T\,R\,T}$$

Partial pressure and mole fraction

$$X_i = \frac{n_i}{n_T}, \qquad \sum X_i = 1$$

$$\mathrm{P_T V = n_T RT}\text{------}\mathbf{1}$$

$$\mathrm{P_i V = n_i RT}\text{------}\mathbf{2}$$

By dividing 2 by 1 :

$$P_i = X_i . P_T$$

Processes and Cycles

Any change a system undergoes from one equilibrium state to another is called a process, and the series of states through which a system passes during a process is called a path.

Quasi-equilibrium process: can be viewed as a sufficiently slow process that allows the system to adjust itself internally and remains infinitesimally close to an equilibrium state at all times. Quasi-equilibrium process is an idealized process and is not a true representation of the actual process. We model actual processes with quasi-equilibrium ones. Moreover, they serve as standards to which actual processes can be compared.

Process diagrams are used to visualize processes. Note that the process path indicates a series of equilibrium states, and we are not able to specify the states for a non-quasi equilibrium process.

Prefix **iso-** is used to designate a process for which a particular property is constant.

- Isothermal: is a process during which the temperature remains constant **T = Cte**
- Isobaric: is a process during which the pressure remains constant **P = Cte**
- Isometric: is process during which the specific volume remains constant V = Cte, W = 0.

Also, in thermodynamics, an **adiabatic process** is a type of thermodynamic process that occurs without transferring heat or mass between the thermodynamic system and its environment.

A system is said to have undergone a cycle if it returns to its initial state at the end of the process.

The zeroth law of Thermodynamics. If **A**, **B** and **C** are different thermodynamical systems and A is in thermodynamical equilibrium with **B** and **B** is in thermodynamical equilibrium with **C**, then **A** is in thermodynamical equilibrium with **C**.