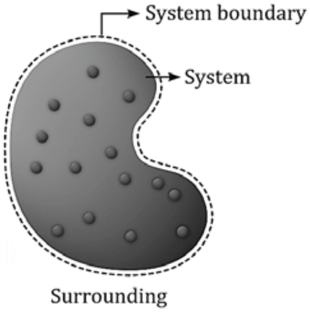
# Chapter 18

# Thermodynamics

## THERMODYNAMICS SYSTEM AND ITS CHARACTERISTICS

### Thermodynamic System

A thermodynamic system is a distinct portion of matter delineated by a definite boundary, within which processes are to be analyzed.



### Surroundings

The surroundings encompass all entities that interact with the system.

### Boundary

Boundaries demarcate the system from its surroundings. These boundaries can be real or conceptual, as well as rigid or flexible.

### Universe

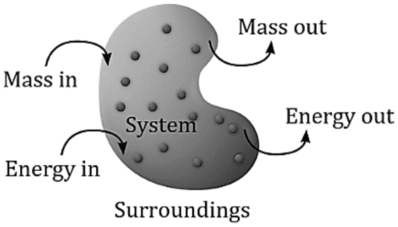
Both the system and its surroundings collectively constitute the universe.

### Types of System and its Characteristics

Thermodynamic systems are categorized based on the potential interactions between the system and its surroundings.

### Open system

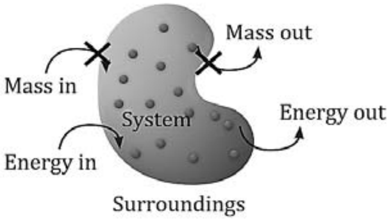
In an open system, both mass and energy are exchangeable between the system and its surroundings.



- Isobaric, Isothermal and Adiabatic Process
    1. Isobaric process and its characteristics
    2. Isothermal process and its Characteristics
    3. Adiabatic process and its Characteristics
- Thermodynamic Process
    1. Graphical Analysis and comparison of general processes in Thermodynamics
    2. Numerical from Graphical Analysis
- Second law of thermodynamics
    1. Heat engine
    2. Efficiency of heat engine
    3. Carnot cycle and efficiency
    4. Coefficient of performance

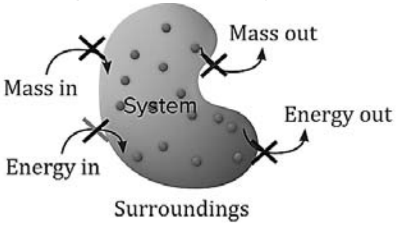
**Closed system**

In a closed system, energy is the sole entity transferred between the system and the surroundings, with no exchange of mass.



**Isolated system**

In an isolated system, neither mass nor energy can be exchanged between the system and its surroundings.



| Types of system | Mass interaction | Energy interaction |
|---|---|---|
| Open system | Allowed | Allowed |
| Closed system | Not allowed | Allowed |
| Isolated system | Not allowed | Not allowed |

**Ex.** Water is being poured in a tank through its inlet while the tank supplies water through its outlet. The rate of flow on both the ends is such that the level of water in the tank does not change. This is an example of which of the following systems?

(A) Open system (B) Closed system

(C) Isolated system (D) None of the above

**Sol.** In this example, the water is continuously moving in and out of the system. So, there is a mass – energy interaction happening. Therefore, it is an open system.

Thus, option (A) is the correct answer.

**Thermodynamic Views**

**Microscopic view**

- ➢ Consideration is given to events taking place at the molecular level.
- ➢ Understanding the behavior of individual particles is necessary for analyzing the system.

**Macroscopic view**

- ➢ Events at the macroscopic level (across all systems) are considered, while molecular-level events are disregarded.
- ➢ Understanding the collective behavior of individual particles is necessary for studying the system.

**Thermodynamic Properties**

- ➢ **Intensive properties**

  Intensive properties are physical properties of a substance that remain unchanged regardless of the size or quantity of material in the system.

  Ex. Temperature, density, and pressure etc.
- ➢ **Extensive properties**

  Extensive properties are physical characteristics of a substance that vary based on the size and quantity of material within the system.

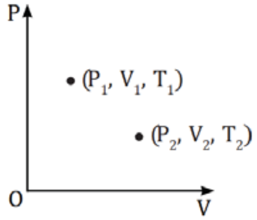
  Ex. Mass, volume, and energy etc.

## Thermodynamic Coordinate System

In thermodynamics, the typical properties of a system, particularly in gaseous systems, are pressure (P), volume (V), and temperature (T).

These constitute the thermodynamic coordinates, defining the state of a system. With these coordinates, an indicator diagram, such as a P-V graph, can be constructed to represent the system.

Now, consider a system wherein a substance undergoes heating from an initial state characterized by pressure $P_1$, volume $V_1$, and temperature $T_1$, to a final state characterized by pressure $P_2$, volume $V_2$, and temperature $T_2$. Employing the thermodynamic coordinate system, both states can be defined as points on the P-V graph, as depicted in the figure.



## Ideal Gas and Universal Gas constant

### Ideal Gas

Here are some fundamental rules concerning ideal gases:

1. The molecules continuously move in random directions.
2. Molecules exhibit behavior similar to that of rigid spheres.
3. All collisions are elastic.
4. Pressure arises from collisions between molecules and the container walls.

### Universal Gas Constant

For an ideal gas,

$$PV = NkT$$

Where, $k = 1.38 \times 10^{-23} JK^{-1}$

If a gas contains n moles, $N = nN_A$ (where $N_A =$ Avogadro's number $= 6.023 \times 10^{23}$ )

$$PV = nN_AkT$$
$$PV = nRT$$

Universal gas constant, $R = N_Ak$

$$R = 8.314 JK^{-1}\text{ mol}$$

### Characteristic Gas Constant

From the ideal gas equation,

$$PV = nRT$$
$$PV = \frac{m}{M}RT$$
$$PV = mR_CT$$

Where,$R_C = \frac{R}{M} =$ Characteristic gas constant

Characteristic gas constant of air,

$$R_{C_{alr}} = \frac{8.314}{29}$$
$$R_{C_{alr}} = 0.287 \times 10^3 JKg^{-1}K^{-1}$$

## Conservation of Energy

Energy cannot be created or destroyed; it can only be transformed from one form to another.

## Specific Heat of a Gas

### Specific heat at constant volume

The specific heat at constant volume is the amount of heat needed to increase the temperature of a unit mass of gas by 1 °C or 1 K while keeping its volume constant.

$$c_V = \frac{(\Delta Q)_V}{M \times \Delta T}$$

### Molar specific heat at constant volume

The molar specific heat at constant volume refers to the amount of heat needed to increase the temperature of one mole of a gas by 1 °C or 1 K while maintaining its volume constant.

$$C_V = M_{molar}\, c_V$$
$$C_V = M_{molar}\left(\frac{(\Delta Q)_V}{M \times \Delta T}\right)$$
$$C_V = \frac{1}{n}\frac{(\Delta Q)_V}{\Delta T}\left(\text{ Since } n = \frac{M}{M_{molar}}\right)$$

### Specific heat at constant pressure

The specific heat at constant pressure is the amount of heat needed to increase the temperature of a unit mass of a gas by 1 °C or 1 K while keeping its pressure constant.

$$c_P = \frac{(\Delta Q)_P}{M \times \Delta T}$$

### Molar specific heat at constant pressure

The molar specific heat at constant pressure refers to the amount of heat needed to increase the temperature of one mole of a gas by 1 °C or 1 K while maintaining its pressure constant.

$$C_P = M_{molar}\, c_P$$

$$C_P = M_{molar}\, (\frac{(\Delta Q)_P}{M \times \Delta T})$$

$$C_P = \frac{1}{n}\frac{(\Delta Q)_P}{\Delta T} (\text{ Since } n = \frac{M}{M_{molar}})$$

### Mayer's formula

The relationship between molar specific heat at constant volume and molar specific heat at constant pressure is termed as Mayer's formula or Mayer's relation.

Mayer's formula establishes the relationship between molar specific heat at constant volume ($C_V$) and molar specific heat at constant pressure ($C_P$) as follows:

$$C_P - C_V = R$$

Where, R is the universal gas constant.

Therefore, from Mayer's formula it can be easily be concluded that $C_P > C_V$ since R is a positive quantity.

### Specific heat in terms of the degree of freedom

Heat supplied to a gas at constant volume, $\Delta Q_V = nC_V\Delta T$

If f represents the degrees of freedom, then the molar specific heat at constant volume ($C_V$) is expressed as:

$$C_V = (\frac{1}{2}f)R$$

Also from Mayer's formula, $C_P - C_V = R$

Therefore, $$C_P = C_V + R$$

$$C_P = \frac{f}{2}R + R$$

$$C_P = (\frac{f}{2} + 1)R$$

### Adiabatic index (γ)

The adiabatic index is defined as,

$$\gamma = \frac{C_P}{C_V}$$

Also, $$C_V = \left(\frac{1}{2}f\right) R \text{ and } C_P = \left(\frac{f}{2} + 1\right) R$$

$$\gamma = \frac{C_P}{C_V} = \frac{\left(\frac{f}{2}+1\right)R}{\left(\frac{1}{2}f\right)R}$$

$$\gamma = \left(1 + \frac{2}{f}\right)$$

### Value of γ for different gases

**1.** For a monatomic gas,
$f = 3$
$\gamma = \frac{5}{3} = 1.6$

**2.** For a diatomic gas,
$f = 5$
$\gamma = \frac{7}{5} = 1.4$

**3.** For a triatomic gas
$f = 6$ (non linear)
$\gamma = \frac{4}{3} = 1.33$