BASICS OF THERMODYNAMICS

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Definition of Thermodynamics

- *Thermodynamics* is a Greek word which means flow of heat in physical and chemical reactions
- Thermodynamics is a branch of science which deals with study of different forms of energy and their interconversions
- It deals with energy changes in physical and chemical processes

Importance of thermodynamics

- Useful to predict whether any chemical reaction can occur under specified conditions
- Used to predict the extent of chemical reaction before equilibrium is reached
- Used to derive important laws like Law of equilibrium.

Terms used in Thermodynamics

System

- May be defined as *the part of universe selected for thermodynamic consideration i.e. to study the effect of temperature, pressure etc.*
- It may also be defined as *specified part of universe in which energy changes are taking place*

Terms used in Thermodynamics

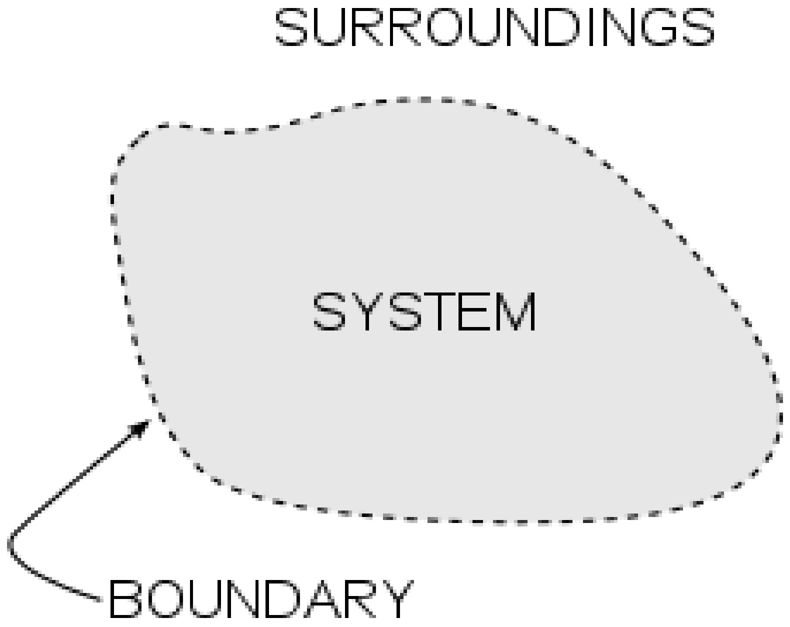
Surrounding

- *The remaining portion of universe excluding the system is called Surrounding*

- **Universe = System + Surrounding**

- The System And Surrounding can be separated by real and imaginary boundary

Terms used in Thermodynamics

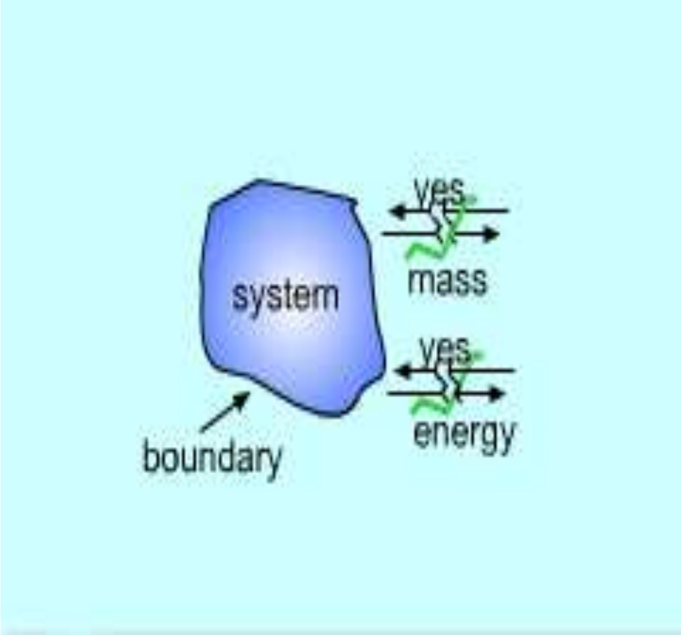


Terms used in Thermodynamics

Types of System

1. Open System: Here mass and energy can be exchanged with surroundings eg. If some water is kept in open vessel or hot tea in open cup

Open System



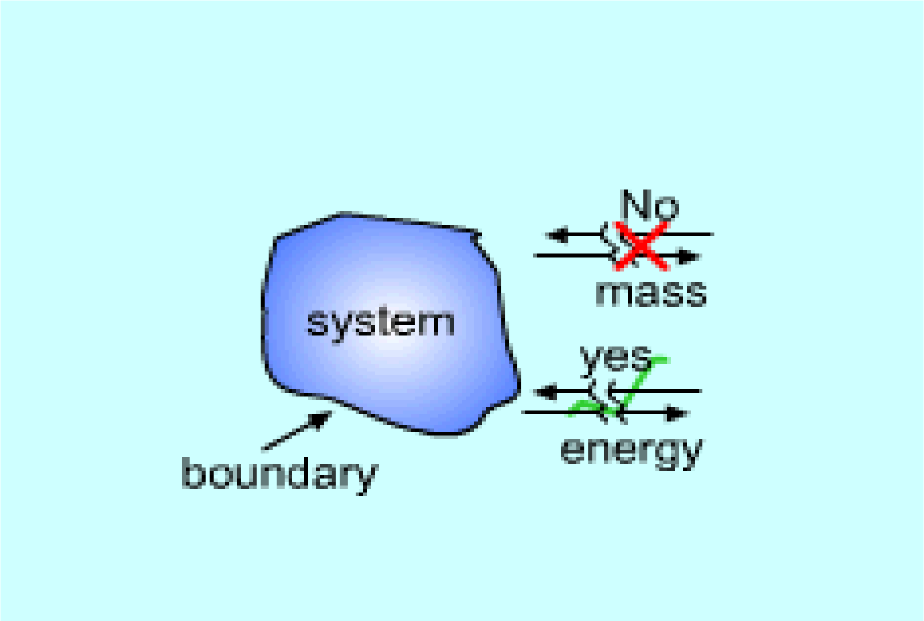
Terms used in Thermodynamics

2.Closed System

In a closed system, there is only the exchange of energy with surroundings, no exchange of mass takes place

For example, if water is placed in closed metallic vessel or hot tea placed in closed tea pot.

Closed system



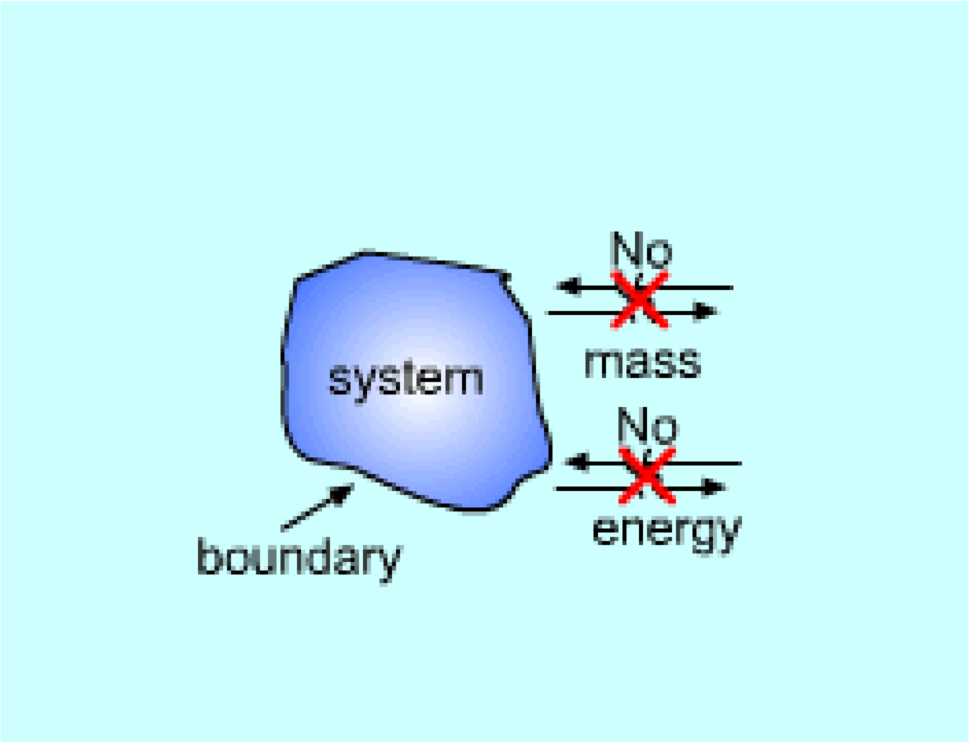
Terms used in Thermodynamics

3. Isolated System

There is neither exchange of mass nor energy with surrounding.

Eg. Water placed in a vessel which is closed as well as insulated or tea placed in a thermos flask

Isolated System



Terms used in Thermodynamics

Classification of system on the basis of nature of constituents

- ***Homogenous System***: All the constituents are present in the *same* phase and *composition of system is uniform throughout*
- **Heterogenous System**: It contains *two or more phases* and *the composition is uniform throughout*

Intensive and Extensive Properties

Intensive Properties

- They *do not depend on the size of the system or quantity of matter present in it*.
- They are dependent on the nature of substance present in it.
- Example: pressure, temperature, density, surface tension

Intensive and Extensive Properties

Extensive Properties

- *Depend on the Quantity of matter present in the system*
- Examples: volume, energy, heat capacity, entropy

State of system and State Variables

State of System

- They are the *condition of system* which is described in terms of certain measurable properties such as temperature(T), pressure(P), volume(V) etc. of the system.

State of system and State Variables

- **State Variables**

  The properties of system such as temperature(T), pressure(P), volume(V) when changed ,the system also changes. These properties are called state variables

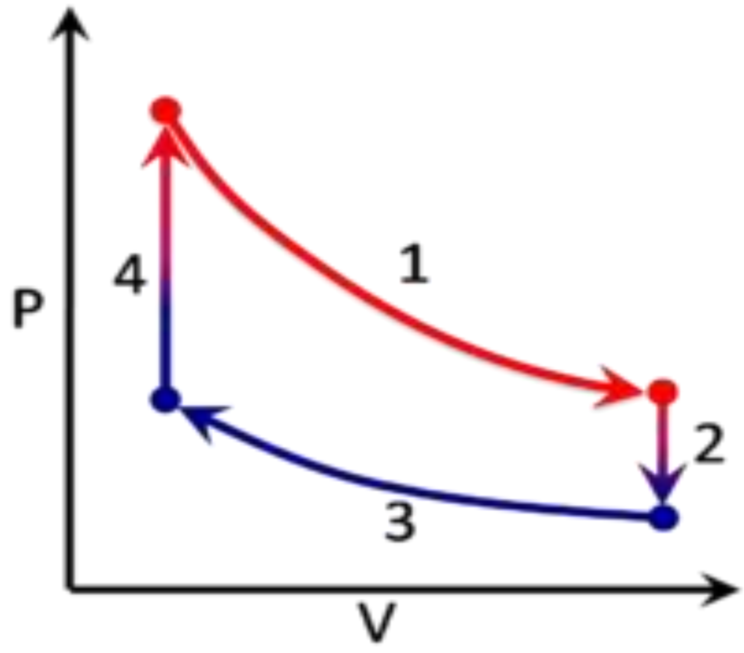
State function

- It is defined as the property whose value *depends only upon the state of the system and is independent of the path by which state has been reached*
- For example: a person standing on the roof of the building has a fixed value of potential energy and the potential of person does not depend whether he has reached there by stairs or lift. Ex. *Potential energy, pressure, volume, temperature, internal energy etc*.

Process

- When state of system changes then ***process*** is said to occur
- the *first* and *last* state of process are called *initial* and *final* state respectively

Process



Process

- Process give us the path by which system changes from one state to other

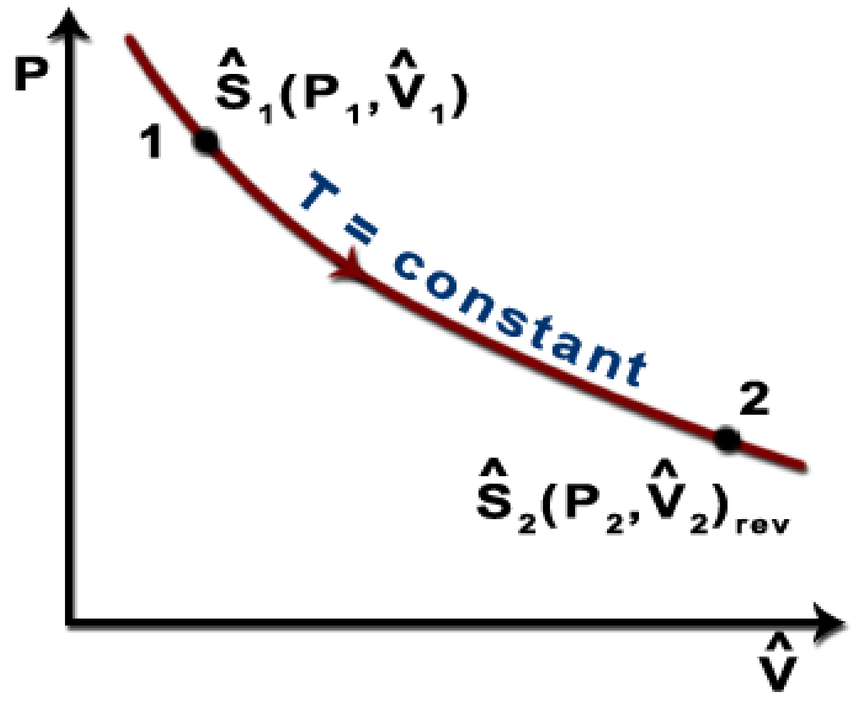
- There are certain processes in which particular state variable is kept constant

Types of Process

Isothermal Process:

- It is defined as the process in which temperature of system remains constant.
- Heat can flow from system to surrounding and vice versa in order to keep the temperature constant

Isothermal process



Types of Process

Adiabatic Process

- The system does not exchange heat with the surrounding
- System is completely insulated from surrounding

Types of Process

Isochoric Process:

- Volume of system remains constant during the process

Types of Process

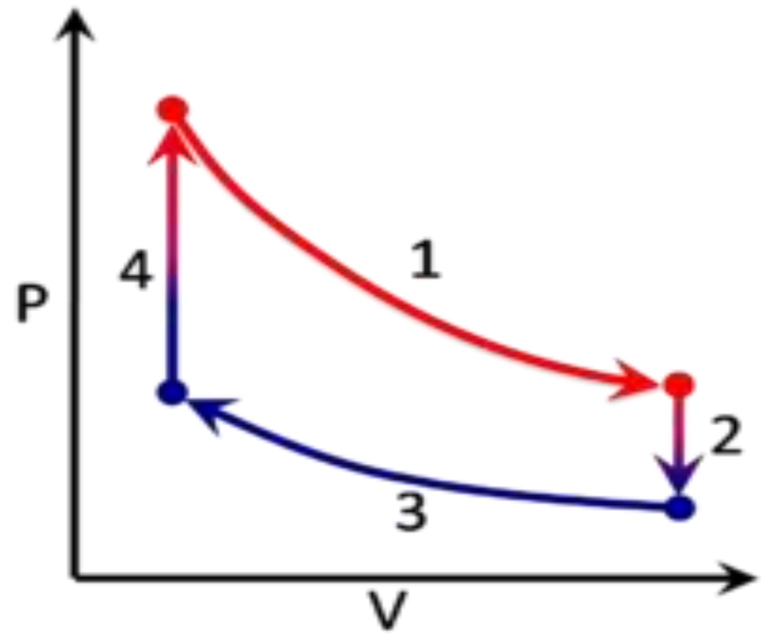
Isobaric Process:

- Here pressure of the system remains constant during the process

Cyclic Process

- Here the system undergoes series of changes and finally returns to its initial state

Cyclic Process



Reversible Process

- Such a process is carried out infintesimally slowly so that all changes occuring in the direct process can be reversed and the system and the surrounding remain in state of equilibrium
- It is an ideal process and cannot be realized in actual process

- **Irreversible process**
- Change is brought about rapidly and the system does not attain equilibrium
- The force which drives the reactants towards products is greater than opposing force which is to carry reverse process

Spontaneous process

- It may also be defined as the process which can take place by *itself* or *initiation*

Which take place by itself

- Evaporation of water in open vessel
- Dissolution of salt in water
- Flow of water down a hill

Which take place by initiation

- Combination of oxygen and hydrogen to form water
- Lighting of candle is initiated by ignition

Non Spontaneous Process

- It is the process which cannot take place by itself or initiation
- *Examples*:

Flow of heat from cold body to hot body

Flow of water up the hill

Dissolution of sand in water

Some Thermodynamics Quantities

Internal Energy

- Every system is associated with a definite amount of energy, which is called its internal energy. It is donated by E or U
- It depends upon the various factors such as temperature, pressure and chemical nature of the substance

Some Thermodynamics Quantities

Change in Internal Energy

The change in internal energy in a chemical reaction is the difference in the internal energies of the products and the reactants

$\Delta E = E(\text{products}) - E(\text{reactants})$

$= E_p - E_r$

Some Thermodynamics Quantities

- **Enthalpy(H)**

Enthalpy or heat content of a system may be defined as the sum of the internal energy and the product of its pressure and volume

$$H = E + PV$$

Where E is the internal energy

P is pressure

V is the volume of the system

Some Thermodynamics Quantities

Change In Enthalpy

- It is the difference in the enthalpies of the products and the reactants
- ΔH = H(products)- H(reactants)

  = H p- Hr

Some Thermodynamics Quantities

Entropy

- I t is a measure of the randomness or disorder of the system
- The greater the randomness, the greater the entropy
- Entropy of a crystalline substance is *minimum* in the solid state and *maximum* in the gaseous state

Entropy

- Melting of ice is an example of increasing entropy

Some Thermodynamics Quantities

Entropy

- It is represented by S
- It depends on temperature and increases with increase in temperature
- ***The change in entropy*** is equal to heat absorbed isothermally and reversibly during a process divided by absolute temperature at which heat is adsorbed
- $\Delta S = q\ rev/T$

LAWS OF THERMODYNAMICS

There are four Laws of thermodynamics:

- Zeroth law of thermodynamics
- 1^{st} Law of thermodynamics
- 2^{nd} Law of thermodynamics
- 3^{rd} Law of thermodynamics

LAWS OF THERMODYNAMICS

Zeroth Law of thermodynamics

- When two bodies A and B are separately in thermal equilibrium with a third body, they in turn are in equilibrium with each other

LAWS OF THERMODYNAMICS

1st Law of thermodynamics

- Energy can neither be created nor destroyed although it may be converted from one form to other
- The total energy of the universe remains constant although it may undergo tranformation from one form to other
- The energy of an isolated system remains constant

LAWS OF THERMODYNAMICS

- **1st Law of thermodynamics**

$$\Delta U = q + W$$

Where

ΔU = change in internal energy

q = heat energy

W = work done

LAWS OF THERMODYNAMICS

2nd Law of thermodynamics

- All spontaneous or naturally occuring processes are irreversible
- Without the help of an external agency a spontaneous process cannot be reversed thermodynamically
- The entropy of an isolated system must increase if it is to be spontaneous

LAWS OF THERMODYNAMICS

- **2^{nd} Law of thermodynamics**
- In an non isolated system the total energy of both the system and surrounding must increase or must be positive
- The total entropy of the universe must tend to increase in a spontaneous process
- ΔS (total) = ΔS system + ΔS surrounding

LAWS OF THERMODYNAMICS

3rd Law of thermodynamics

- The entropy of all perfectly crystalline solids may be taken as zero at the absolute temperature
- At absolute zero a perfectly crystalline solid has a perfect order of its constituent particles i.e. there is no disorder at all. Hence absolute entropy is taken as zero

Thank You