Thermodynamics

(Module -1)

B.Sc. III Year

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The word “Thermodynamics” is a Greek word which means, Study of flow of heat. Thermodynamics is a branch of Physical chemistry, which deals with the energy changes accompanying a chemical reaction.

Thermodynamics, describes macroscopic properties of equilibrium systems and Built on 4 Laws of Thermodynamics,

- 0^{th} Law ⇒ Defines Temperature (T) :

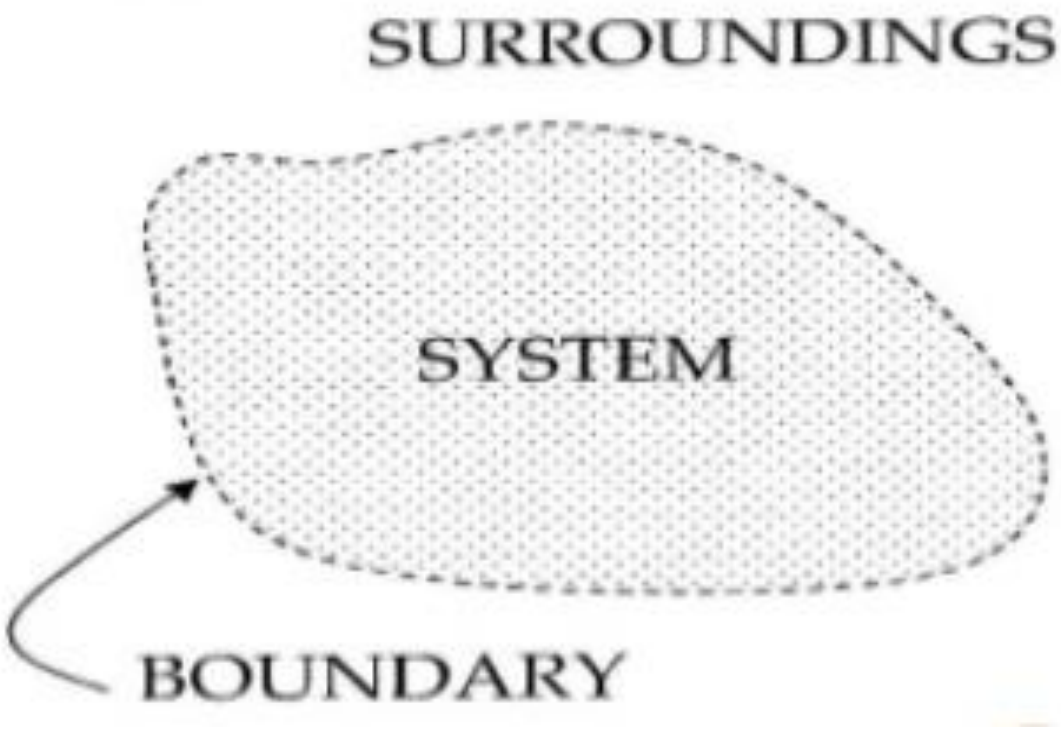
Two bodies which are in thermal equilibrium with a third body are in thermal equilibrium with each other.

- 1^{st} Law ⇒ Defines Energy (U) : The energy of the universe is constant.

- 2^{nd} Law ⇒ Defines Entropy (S) : In any spontaneous process, there is always an increase in entropy of the universe.

- 3^{rd} Law ⇒ Gives Numerical Value to Entropy: The entropy of a perfect crystal at 0 Kelvin is zero.

- System: The part of the Universe that we choose to study
- Surroundings: The rest of the Universe
- Boundary: The surface dividing the System from the Surroundings


SURROUNDINGS
SYSTEM
BOUNDARY

Systems can be:

- Open: Mass and Energy can transfer between the System and the Surroundings
- Closed: Energy can transfer between the System and the Surroundings, but NOT mass
- Isolated: Neither Mass nor Energy can transfer between the System and the Surroundings.

Thermodynamic process

The operation by which a thermodynamic system changes from one state to another is called a thermodynamic process.

A thermodynamic process is always accompanied by change in energy.

Depending upon the condition of change, different types of thermodynamic processes are defined,

Isothermal process

A process in which the temperature of the system remains constant throughout the process, yet heat enters or leaves the system is called as isothermal process. Isothermal processes are carried out by placing the system in a thermostat.

For isothermal processes, change in temperature is zero ($dT = 0$)

Adiabatic process

A process in which no heat enters or leaves the system during any step of the process is known as adiabatic process. Such processes are carried out in closed insulated containers (Thermos bottle).

For adiabatic process, change in heat is zero ($dQ = 0$).

Isobaric process

A process during which pressure of the system remains constant throughout the reaction is known as isobaric process. For isobaric process, $dP = 0$

Isochoric process

A process during which volume of the system remains constant throughout the reaction is known as isochoric process, for which, $dV = 0$.

A reversible process can be proceed very slowly through a succession of infinitesimal steps and its direction can be reversed at any point by making a small change in temperature or pressure.

An irreversible process is carried out in a single step and cannot be carried out in reverse order. All spontaneous processes are irreversible.

THE FIRST LAW OF THERMODYNAMICS

It is also known as Law of conservation of energy.

The first law of thermodynamics states that,

"The energy can neither be created nor be destroyed, but it can be transformed from one form to another form "

Or

"The total amount of energy of the universe is a constant"

Or

The total energy of an isolated system remains constant though it may change from one form to another.

First law of Thermodynamics

Mathematical form of First law of thermodynamics,

$$\Delta E = q + w,$$

Where,

ΔE = Change in internal energy of the system,

q = Amount of heat supplied to the system,

w = Work done on the system

First law of Thermodynamics

If q amount of heat is supplied to a system, then this heat energy is useful in two ways,

When a system goes from initial state to the final state, it undergoes a change in the internal energy from E_1 to E_2, thus, $\Delta E = E_2 - E_1$. The second part is used to do some external work on the system by the surroundings (w), If the work is done by the system on the surroundings, then the first law becomes,

$$\Delta E = q - w$$

SIGN CONVENTIONS

- +q = Heat absorbed by the system,
- -q = Heat liberated by the system
- +w = Work done on the system,
- -w = Work done by the system

Applications of first law of thermodynamics

For Isothermal process

Since temperature remains constant in the isothermal process so the internal energy of the gas must also remain constant, When a system undergoes an isothermal change

(T = Constant) i.e. $\Delta E = 0$, then the first law of thermodynamics becomes, $q = - w$,

i.e. Heat absorbed by the system from the surroundings = work done by the system on the surroundings

Applications of first law of thermodynamics

For isochoric process (V = Constant), w = 0 then $\Delta E = q$, increase in internal energy of the system is equal to the heat absorbed by the system

Applications of first law of thermodynamics

Adiabatic process:

A process in which no heat can enter or leave the system is called an adiabatic process.” In an adiabatic process, there is no transfer of heat across the boundary of the system, so Q=0. For adiabatic process, there is no exchange of heat between the system and the surroundings, q = 0, then ΔE = w, the increase in internal energy of the system is equal to the work done on the system

Applications of first law of thermodynamics

Isolated system: It is a system that does not interact with the surroundings. In this case, there is no heat flow and the work done is zero. It means $\Delta Q = 0$ and $\Delta W = 0$. Hence $\Delta E = 0$. Therefore the internal energy of an isolated system remains constant.

Applications of first law of thermodynamics

Cyclic process: The process in which a system returns to its initial state after passing through various intermediate states is called a cyclic process. In this process, the change in internal energy is zero. i.e., $\Delta U = 0$. Hence from the first law of thermodynamics. $\Delta W = \Delta Q$, Hence, in a cyclic process, the amount of heat given to a system is equal to the net work done by the system.

Limitations to first law of thermodynamics

- The law states that whenever a system undergoes any thermodynamic process it always holds certain energy balance. However, the first law does not specify the feasibility of the reaction
- It does not tells us about direction in which heat flows when they are in contact

Limitations to first law of thermodynamics

- It does not tell about the final temperature of two bodies when they are in direct contact.
- It does not tell about the entropy of system.

THANK YOU……