



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

THERMODYNAMICS

Thermodynamics means “flow of heat”. It is a branch of physical science dealing with quantitative relation between heat and mechanical energy. In broad sense, it basically deals with the relationship of heat to all other forms of energy, light and kinetic energy. The main aim of thermodynamics is to determine the efficiency of the engines. This information is very important for an engineer to design the efficient engines.

Thermodynamic Equilibrium

A system is said to be in a state of thermodynamic equilibrium when its state variables remain constant throughout, i.e., state variables do not change with time and space.



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Characteristics for equilibrium state:

- 1) The temperature remains constant in all parts of the system.
- 2) 2) There is no change to intensive properties of the system with time.
- 3) There is no flow of matter within the system or boundaries.
- 4) No mechanical work is done by the system or done upon the system.
- 5) The chemical property of the system does not change with time.



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Isothermal process is a process carried out at constant temperature. Here the system exchanges its heat with its surroundings.

Adiabatic process is one in which there is no exchange of heat with surroundings. Therefore the temperature of the system may increase or decrease. The system is also insulated.

Isobaric process : In this process there is constant pressure. But volume change always takes place.

Isochoric process is the process where volume of the system is kept constant .



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Reversible process : A process is said to be reversible, when the energy change in each step of the process can be reversed in direction by merely a small change in a variable (like temperature, pressure, etc.,) acting on the system. A system that has undergone a reversible process can be restored back to its original or initial state by infinitesimal change in external system. Daniel cell is the example for reversible process.

Irreversible process : Irreversible process is one in which the system or surroundings are not restored to their initial state at the end of the process. They are also called “Spontaneous processes”. The direction of the process is spontaneous. All the natural process is irreversible in nature.



Internal Energy

Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Every chemical system has some internal energy (E), which is a definite property. It is a function of temperature, chemical nature of the matter and at times the pressure and volume of the system.

The magnitude of the internal energy of a given system of molecules is determined by kinetic, rotational and vibrational movement of molecules and their component atoms as well as by the way in which the molecules are put together, and the nature of the individual atoms.

It is impossible to determine the absolute value of the internal energy of a system. But we can determine the change in internal energy of a system. It is represented by E.

$$\Delta E = E_2 - E_1$$

where,

E₂ = internal energy of system at final state

E₁ = internal energy of a system at initial state.

ΔE is a state function. i.e., it depends on initial and final state of the system but it does not depend upon the path in which the change takes place.



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Mathematical form of First law of Thermodynamics

Statements :

- 1) Energy can neither be created nor destroyed, though it may be converted from one form to another.
- 2) The total energy of isolated system remains constant. Although it may change from one form to another. The heat of a system is denoted by q . If heat is gained by the system, positive sign is given, ($+q$). If heat is lost by the system, negative sign is given, ($-q$).

The work function of a system is denoted by the symbol w .

- If work done by the system on the surroundings, positive sign is given ($+w$);
- If work done is on the system, negative sign is given ($-w$).



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

As per First law of Thermodynamics, Heat supplied to the system is q , a part of this heat is used up to increase the internal energy E and rest is used to perform external work, w .

$$q = \Delta E + w$$

$$\Delta E = q - w \dots 1$$

For infinitesimally small change, the equation (1) may be rewritten as follow

$$dE = dq - dw \dots 2$$

The equation (1) and (2) are mathematical forms of First law.

Note : For a cyclic process,

$$E_1 = E_2 \text{ or } \Delta E = 0$$

$$\text{1st law } \Delta E = q - w = 0$$

$$q = w$$

Here the work done is equal to the heat absorbed in cyclic process.



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Limitations of First law of thermodynamics :

- 1) It does not explain why
 - (a) chemical reactions do not proceed to completion
 - (b) natural (spontaneous) processes are unidirectional.
- 2) It does not explain
 - a) source of heat and direction of heat flow
 - b) the extent of convertibility of one form of energy into another.
- 3) Work can be completely converted to heat, but heat cannot be converted into work. This fact cannot be explained by this law.
- 4) It does not provide information regarding the feasibility of the process.
- 5) It does not explain spontaneous or natural processes.
- 6) It does not explain the diffusion of gases from low pressure to high pressure (or) water itself flow uphill etc.,



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Enthalpy

We know

$$E = q - w \text{ (1st law) } \dots\dots (1)$$

Let us consider a system changes from state A to B at constant pressure (P). The volume increased from V_A to V_B . It absorbs heat 'q' to perform this change.

Then 1st law becomes

$$q = (E_B - E_A) + w \dots\dots (2)$$

(work done by the system on surroundings)

Due to this work the volume changes from V_A to V_B

$$\text{Work done by the system} = P (V_B - V_A) \dots\dots (3)$$

$$q = (E_B - E_A) + P (V_B - V_A)$$

$$q = (E_B + P V_B) - (E_A + P V_A) \dots\dots (4)$$



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

The quantity “ $E + PV$ ” is known as Enthalpy or heat content of the system and it is denoted by “ H ”.

Eqn.(4) becomes

$$q = H_B - H_A = H = q.$$

From the above equation, it is cleared that the enthalpy change H is equal to heat absorbed by (q).

We know, E is a state property (definite) and P and V are also definite properties of a system.

H is also a definite property, depending upon the state of the system. H_A and H_B are definite properties.

Thus ΔH , like ΔE is a definite and state property. From Eqn.(4),

$$\Delta H = (E_B + PV_B) - (E_A + PV_A)$$

$$\Delta H = \Delta E + P\Delta V$$

- i) At constant P , $\Delta H > \Delta E$
- ii) At constant V , $\Delta H = \Delta E$



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Statement of Second law of Thermodynamics

- 1) **Kelvin-Planck statement** : It is impossible to convert the heat completely into an equivalent amount of work, without producing some other changes in some parts of the system.
- 2) **Clausius statement** : It is impossible for a self-acting machine, unaided by any external agency, to convey heat from a body at a lower temperature to a body at a higher temperature.
- 3) **Thomson statement** : The heat of the coldest body among those participating in a cyclic process cannot serve as a source of heat.

Other statements are as follows :

- 4) Heat cannot pass itself from a colder to a hotter body.
- 5) Only a fraction of a given quantity of heat may be converted into work, when it is allowed to flow from a body at a higher temperature to a body at a lower temperature and that its value depends on the temperature difference and the higher temperature.
- 6) It is impossible to convert heat from a reservoir into work by a cyclic process, without transferring it to a colder reservoir.
- 7) All natural or spontaneous process tend to take place in one direction, and they cannot be reversed.
- 8) The energy of the universe is constant, but the entropy approaches a maximum or the universe is approaching a condition of maximum randomness.



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Entropy

Entropy is the quantity that tells whether a chemical reaction or a physical change can occur spontaneously in an isolated system or not. We know that, for a reversible Carnot cycle working between temperatures T_1 and T_2 ($T_2 > T_1$),

we have,

$$q_2 - q_1 / q_2 = T_2 - T_1 / T_2 \dots\dots (1)$$

where,

T_2 = Temperature of heat source and corresponding heat quantity q_2

T_1 = Temperature of heat sink with corresponding heat quantity q_1

$$q_2 / q_2 - q_1 / q_2 = T_2 / T_2 - T_1 / T_2$$



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

$$q_2/q_2 - q_1/q_2 = T_2/T_2 - T_1/T_2$$

$$1 - q_1/q_2 = 1 - T_1/T_2$$

$$q_1/q_2 = T_1/T_2$$

$$q_1/T_1 = q_2/T_2$$

$$q_1/T_1 - q_2/T_2 = 0$$

$$q_1/T_1 + (-q_2/T_2) = 0$$

Now q is not equal to 0, therefore ' q ' is not a state variable function. But $(q/T)_{\text{system}} = 0$ $T_{\text{system}} q$ for a reversible Carnot cycle.

Thus, the algebraic sum of entropies ($=q/T$) in a reversible Carnot cycle is zero.

Any process is carried out reversibly, dq is the amount of heat absorbed by the system from the surroundings at temperature T .

Then the entropy change $dS = dq/T$

The increase in entropy (dS) of a reversible change is equal to the quantity of heat absorbed by the system and divided by the temperature of the system in Kelvin scale.



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

For a system, the change in entropy when it changes from state A to B is,

$$\int dS = \int dq/T$$

$$\Delta S = S_B - S_A = \int dq/T$$

where , S_B and S_A are the entropies of the system in state A and B respectively.

For a adiabatic reversible process,

$$dq = 0$$

$$dS = dq/T = 0 \text{ (or) } S = \text{a constant}$$

“Entropy may also be defined as the thermal property of the substance which remains constant during an adiabatic cyclic change

Unit : Joule degree -1 (J K -1)

Actually it is difficult to define the entropy of a system. But it is convenient to define the change of entropy of a system during a change of state.

“The change of entropy of a system may be defined as the integral of all the terms involving heat absorbed (q) divided by the Kelvin temperature (T) during each infinitesimally small change of the process carried out reversible.



Note :

Madan Mohan Malaviya University of Technology, Gorakhpur-273010

$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$ (Reversible process)

$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$ (Irreversible process)

Entropy change in reversible process

Case – I : When the reversible process is isothermal .

Let us consider in a reversible isothermal process, the system absorbs heat 'q' from the surroundings at temperature 'T'.

The increase in the entropy of the system is given by $\Delta S_{\text{system}} = + q_{\text{rev}}/T$

Now, during the same time, the surroundings lose the same quantity of heat 'q' at the same temperature. Thus, there is a decrease of surroundings entropy.

Let it be $\Delta S_{\text{surroundings}} = -q/T$.

Total change in entropy of the process = $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$$\Delta S_{\text{process}} = q/T + (-q/T) = 0$$

i.e., the entropy change in a reversible isothermal process is zero.



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Case II : When the reversible process is adiabatic,

there is no transfer of heat from system to surroundings or vice versa.

$$q = 0$$

$$\Delta S_{\text{system}} = q/T \quad q = 0/T = 0$$

$$\Delta S_{\text{surroundings}} = q/T = 0/T = 0$$

$$\text{Hence } \Delta S_{\text{process}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0 + 0 = 0$$

The entropy change in a reversible adiabatic process is zero.



Madan Mohan Malaviya University of Technology, Gorakhpur-273010

Entropy change in an irreversible process

Let us consider a system at higher temperature T_1 and its surroundings at lower temperature T_2 . Let a quantity of heat 'q' is absorbed irreversibly from the system to surroundings. Then,

Decrease in entropy of system (ΔS_{system}) = $-q/T_1$

Increase in entropy of surroundings $\Delta S_{\text{surroundings}} = -q/T_2$

Net entropy change in the process = $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

If $T_1 > T_2$ then $T_1 - T_2 = \text{positive}$

$$\Delta S_{\text{process}} = + \text{ve}$$

$$\text{(or)} \Delta S_{\text{process}} > 0$$

i.e., entropy increases in an irreversible process.