Thermodynamics

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Thermodynamics

- Thermodynamics comes from the Greek words therm (heat) and dynamis (power) most descriptive of early attempts to convert heat.

- Thermodynamics is the field of science which deals with the energies possessed by gases and vapours.

- Basically it deals with the relationship between heat, work, temperature, and energy.

- It also includes the conversion of these energies in terms of heat and mechanical work, and their relationship with properties of the System.

- A machine, which converts heat into mechanical work or vice versa, is known as Heat Engine

Thermodynamic system and Classification

■ Thermodynamic system may be defined as a definite area or a space where some thermodynamic process is taking place.

■ The thermodynamic systems may be classified
into the following three groups:
1. Closed system
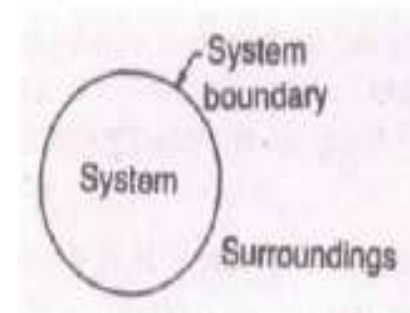2. Open system
3. Isolated system

Fig-Thermodynamic System

■ **Closed system:**
✓ A system of fixed mass and identity
whose boundaries are determined by
the space of the matter occupied in it.

✓ In Fig, if heat is supplied to the cylinder, the
temperature of the gas will increase and the
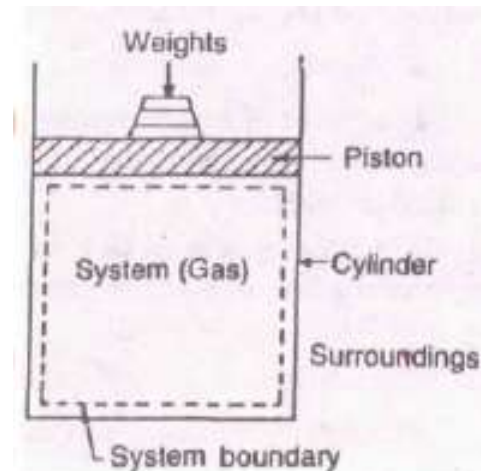piston will rise and the boundary of the
system moves.

Fig- Closed System

Cont.

✓ No addition or loss of the original mass of the working substance.

✓ Thus, a closed system does not permit any mass transfer across its boundary, but it permits transfer of energy (heat and work).

■ **Open system:**

✓ The mass of the working substance crosses the boundary of the system. Heat and work may also cross the boundary.

✓ The fig Shows the diagram of an air compressor which indicates an open system.

✓ The working substance crosses the boundary of the system as the low pressure (L.P.) air enters the compressor and leaves the high pressure (H.P.) air.
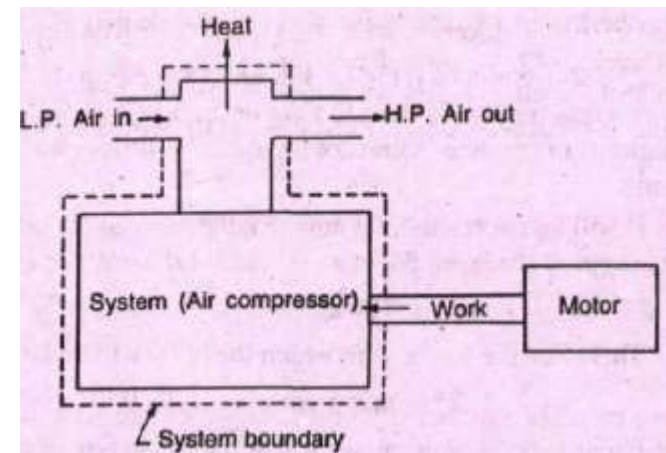
Cont.

- The mass of working substance within the system may not be constant.

- **<u>Isolated system:</u>**

✓ A system which is completely uninfluenced by the surrounding is called an isolated system.

✓ It is a system of fixed mass and no heat or work energy cross its boundary. The practical examples of isolated systems are rare.

✓ The concept of this system is particularly useful in formulating the principles derived from the Second Law of Thermodynamics.

Laws of thermodynamics

■ **Laws of Thermodynamics**

The three laws of thermodynamics are-

1. Zeroth law of thermodynamics
2. First law of thermodynamics
3. Second law of thermodynamics.

■ **Zeroth Law of Thermodynamics:**

"When two systems are each in thermal equilibrium with a third system, then the two systems are also in thermal equilibrium with one another."

-This law provides the basis of temperature measurement.

■ **First Law of Thermodynamics**

✓ "The heat and mechanical work are mutually convertible".

-when a closed system undergoes a thermodynamic cycle, the net heat transfer is equal to the net work transfer.

$$\oint \delta Q = \oint \delta w$$

First Law of thermodynamics

Where $\oint$ =integral around a complete cycle,

δQ and δW = infinitesimal element of heat and work

✓ "The energy can neither be created nor destroyed though it can be transformed from one form to another".

-when a system undergoes a change of state, then both heat transfer and work transfer takes place. The net energy transfer is stored within the system and is known as stored (total) energy of the system.

$$\delta Q - \delta w = dE$$

Where δ is used for a quantity which is inexact differential.

d is used for a quantity which is an exact differential.

E indicates total energy of system.

Limitations of First Law of thermodynamics

■ **Limitations of First Law of thermodynamics-**

✓ *"The net heat transfer is equal to the net work transfer"*

-This statement does not specify the direction of flow of heat and work . It also does not give any condition under which these transfers take place.

✓ *"*The heat energy and mechanical work are mutually convertible"

-Though the mechanical work can be fully converted into heat energy, but only a part of heat energy can be converted into mechanical work.

-It means that there is a limitation on the conversion of one form of energy into another form.

Second Law of Thermodynamics

- **<u>Second Law of Thermodynamics</u>**

   "Entropy of an isolated system always increase over time"

- ✓ According to **Kelvin-Planck** 'It is impossible to construct an engine working on a cyclic process, whose sole purpose is to convert heat energy from a single thermal reservoir into an equivalent amount of work"

   -It means that there is a degradation of energy in the process of producing mechanical work from the heat supplied.

- ✓ According to **Clausius** statement "It is impossible for a self acting machine, working in a cyclic process, to transfer heat from a body at a lower temperature to a body at a higher temperature without help of an external agency(expenditure of mechanical work)"

Thermodynamic Processes

■ **Thermodynamic Process**

When a system changes its state from one equilibrium state to another equilibrium state, then the path of successive states through which the system has passed, is known as a thermodynamic process.
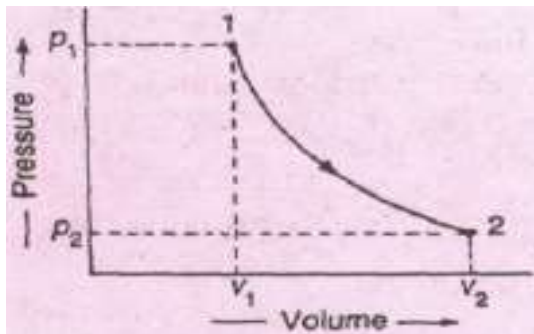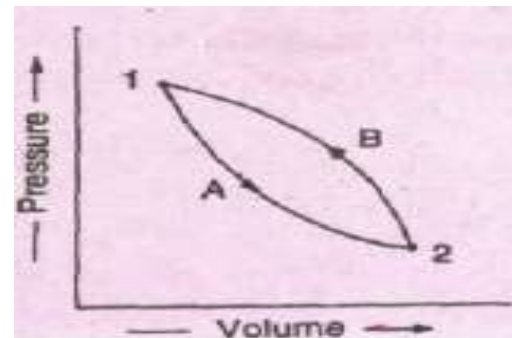

Fig: Thermodynamic Process

Fig: *Thermodynamic Cycle*

■ **Thermodynamic Cycle or Cyclic Process**

When a process or processes are performed on a system in such a way that the final state is identical with the initial state, it is then known as a *thermodynamic cycle or cyclic process. In Fig,* l-A-2 and *2-B-l are processes.*

Reversible and irreversible process

- **Reversible Process (Quasi-static process)-** If a process is assumed to take place sufficiently slowly so that the deviation of the properties at the intermediate states is infinitesimally small, then every state passed through by the system will be in equilibrium. Such a process is called quasi-static or reversible process.

(a) Reversible process.   (b) Irreversible process.
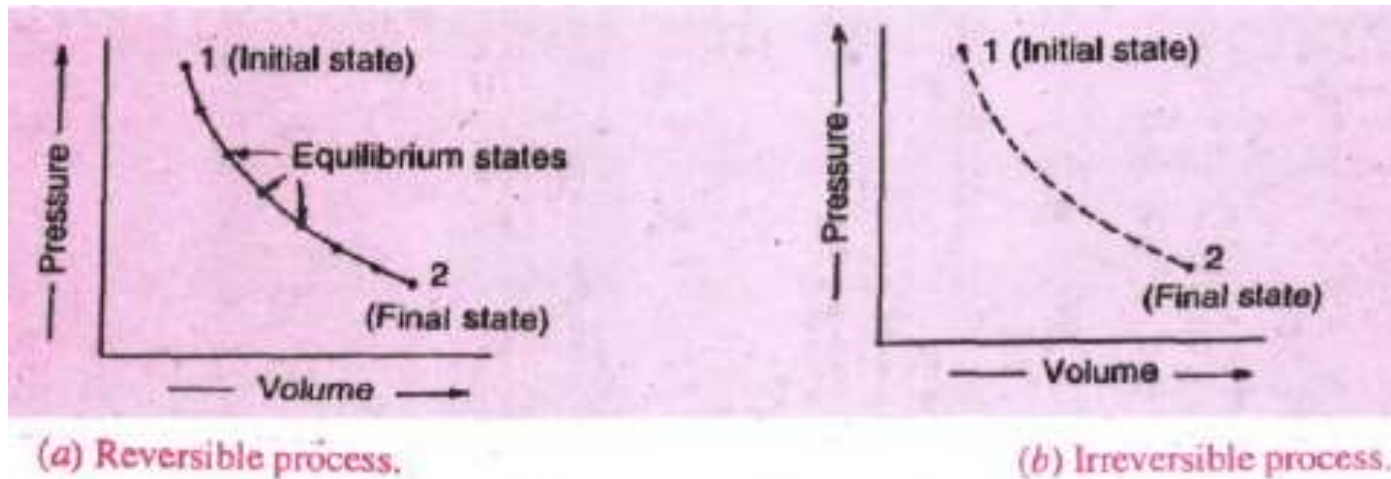
- **Irreversible process -** If the process takes place in such a manner that the properties at the intermediate states are not in equilibrium state, then the process is said to be non-equilibrium / non quasi static/ irreversible process.

Cont.

- **Reversible Vs Irreversible / Quasi Static Process Vs Non-quasi static process-**

S.No.	Reversible process	Irreversible process
1.	It takes place in infinite number of infinitesimally small steps and it would take infinite time to occur.	It takes place in a single step.
2.	It is imaginary as it assumes the presence of frictionless and weightless piston.	It is real and can be performed actually.
3.	It is in the state of equilibrium at all the stages of operation.	It is in equilibrium state only at the initial and final stages of the operation.
4.	All changes are reversed when the process is carried out in reversible direction.	After the occurring of the process changes do not return to the initial state by themselves.
5.	It is extremely slow.	It proceeds at measurable speed.
6.	Work done by a reversible process is greater than the corresponding irreversible process.	Work done in irreversible process is smaller than the corresponding reversible process.

Specific Heat

- **<u>Specific Heat-</u>**

✓ Specific heat is defined as the amount of heat required to raise the temperature of a unit mass of any substance by one degree. It is generally denoted by c.

✓ Gases have the following two specific heats depending upon the process adopted for heating the gas-

     1. Specific heat at constant pressure (Cp), and

     2. Specific heat at constant volume (Cv)

✓ <u>Cp</u> is the amount of heat required to raise the temperature of a unit mass of a gas through one degree, when it is heated at constant pressure.

✓ <u>Cv</u> is the amount of heat required to raise the temperature of a unit mass of gas through one degree when it is heated at a constant volume.

C*p* and C*v*

- **Relation between Specific Heats (C*p* and C*v*)**
- ✓ Consider a gas enclosed in a container and being heated, at a constant pressure, from the initial state 1 to the final state 2. Now heat supplied to the gas at constant pressure,

$$Q_{1-2} = mC_p(T_2 - T_1) \qquad \text{............ (i)}$$

- ✓ A part of this heat is utilised in doing the external work, and the rest remains is used in increasing the internal energy of the gas.

Let m = Mass of the gas,

T_1 = Initial temperature of the gas,

v_1 = Initial volume of the gas,

v_2 = Final volume of the gas,

C_p = Specific heat at constant pressure,

C_v = Specific heat at constant volume, and

p = Constant pressure.

Heat utilised for external work,

$$W_{1-2} = p(v_2 - v_1) \qquad \text{..................... (ii)}$$

and increase in internal energy,

$$dU = mC_v(T_2 - T_1) \qquad \text{.................... (iii)}$$

- ✓ We know $\quad Q_{1-2} = W_{1-2} + dU$

$$\therefore mC_p(T_2 - T_1) = p(v_2 - v_1) + mC_v(T_2 - T_1) \text{ .....(iv)} \quad \text{[From (i), (ii) \& (iii)]}$$

Cont.

✓ Using Characteristic gas equation, we have

$$pv_1 = mRT_1 \quad \ldots\ldots\ldots \text{ (Initial Conditions)}$$

$$pv_2 = mRT_2 \quad \ldots\ldots\ldots \text{ (Final Conditions)}$$

$$\therefore p(v_1 - v_2) = mR(T_2 - T_1) \quad \ldots\ldots \text{ (v)}$$

✓ Substituting the value of $p(v_2 - v_1)$ in equation (iv)

$$mC_p(T_2 - T_1) = p(v_2 - v_1) + mC_v(T_2 - T_1)$$

$$\text{or, } mC_p(T_2 - T_1) = mR(T_2 - T_1) + mC_v(T_2 - T_1)$$

$$\therefore C_p = R + C_v$$

$$\text{or, } C_p - C_v = R$$

Enthalpy

- **<u>Enthalpy-</u>**
- ✓ A thermodynamic quantity equivalent to the total heat content of a system.
- ✓ It is the Sum of the internal energy (U) and the product of pressure and volume (pv) which is known as Enthalpy (H= U+pv).

- ✓ Since *(U+pv) is made up entirely of properties, therefore enthalpy (H) is also a property.*

    For a unit mass, specific enthalpy, $h = u + pv_s$

    Where
    u=Specific internal energy
    v_s=Specific volume

- ✓ We know that $Q_{1-2} = dU + W_{1-2}$

    $$= dU + pdv$$

- ✓ When gas is heated at constant pressure from an initial condition 1 to a final condition 2, then change in internal energy,

    $$dU = U_2 - U_1$$

- ✓ and work done by the gas, $W_{1-2} = pdv = p(v_2 - v_1)$

Cont.

■ Substituting these values,

$$\therefore \quad Q_{1-2} = dU + W_{1-2} = (U_2 - U_1) + p(v_2 - v_1)$$
$$= (U_2 + pv_2) + (U_1 + pv_1)$$
$$= H_2 - H_1$$

■ Thus, for a constant pressure process, **the heat supplied to the gas is equal to the change of enthalpy.**

■ **Internal Energy-**

Internal Energy is the total of the kinetic energy due to the motion of molecules and the potential energy associated with the vibrational motion and electric energy of atoms within molecules

Entropy

■ Entropy is defined as the measure of the thermal energy of a system per unit temperature which is not available for doing work.

$$dS = \frac{\delta Q}{T}$$

Where T= absolute temperature
dS = Increase in entropy
δQ = Heat absorbed

■ Measure of disorder of a system.

■ **Available Heat Energy (A.H.E):** The part of the heat energy which can be converted into mechanical work.

■ **Unavailable Heat Energy (U.H.E):** The part of the heat energy which can not be converted into mechanical work.

■ Heat rejected by the system to surrounding is also known as U.H.E.

∴ Total Heat Supplied to the system,

$$\delta Q = A.H.E + U.H.E$$
$$= Work\ done + Heat\ rejected$$

Now,

$$Efficiency, \eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} \quad \cdots\cdots (1)$$

Where T_1 = Maximum absolute temperature

T_2 = Lowest absolute temperature

Cont.

We also know that efficiency

$$\eta = \frac{\text{Maximum work obtained}}{\text{Heat supplied or absorbed}} = \frac{\delta W}{\delta Q} \dots \dots \dots \dots \dots (2)$$

From equations (1) and (2),

$$\frac{\delta W}{\delta Q} = 1 - \frac{T_2}{T_1}$$

$$\text{or,} \delta W = \delta Q \left(1 - \frac{T_2}{T_1}\right)$$

Since the lowest practical temperature of heat rejection is the temperature of surroundings $(T_2 = T_0)$, then

$$\delta W = \delta Q \left(1 - \frac{T_0}{T_1}\right)$$

$$= \delta Q - \delta Q \times \frac{T_0}{T_1} \dots \dots \dots \dots (3)$$

We also know that work done,

$$\delta W = \text{Heat supplied - Unavailable heat energy or heat rejected.}$$

$$= \delta Q - U.H.E \dots \dots \dots \dots \dots (4)$$

From equations (3) and (4),

$$\delta Q - \delta Q \times \frac{T_0}{T_1} = \delta Q - U.H.E$$

Cont.

$$\text{or,} \qquad \text{U.H.E} = T_0\left(\frac{\delta Q}{T_1}\right) = T_0 \times dS$$

Thus, **change in entropy may be regarded as a measure of unavailable form of heat energy or irreversibility of the process**.

- Enthalpy Vs Entropy

Enthalpy	Entropy
Enthalpy is the sum of internal energy and flows energy.	Entropy is the measurement of the randomness of molecules.
It is a kind of energy. Its unit is $Jmol^{-1}$.	It is a property. Its unit is JK^{-1}.
Enthalpy is positive for endothermic processes.	Entropy is positive for spontaneous processes.
Enthalpy is negative for exothermic processes.	Entropy is negative for non-spontaneous processes.
The system favour minimum enthalpy.	The system favour maximum entropy.

Classification of Thermodynamic processes

- All the thermodynamic processes are classified into the following two groups-
    1. Non-flow processes and
    2. Flow processes
- **Non-flow processes-** The processes occurring in closed systems which do not permit the transfer of mass cross their boundaries, are known as non-flow processes.
- ✓ The energy crosses the system boundary in the form of heat and work.

- **Flow processes-** The processes occurring in open systems which permit the transfer of mass to and from the system, are known as *flow processes.*
- ✓ The mass enters the system and leaves after enhancing energy.

- ✓ The flow processes may be
    - ✓ **Steady flow process-** (examples- flow through nozzles, turbines, compressors etc)
    - ✓ **Non-steady flow processes-** (examples -filling or evacuation of vessels)

Non-flow Processes

■ Different non-flow processes (Reversible and irreversible) are applied for heating and expansion of gas-

1 . **Reversible non-flow processes-** These processes are as follows :

➢ **Isochoric process-** A process with no change in volume of the system.
➢ **Isobaric process-** A process with no change in pressure of the system.
➢ **Isothermal process-** A process with no change in temperature of the system.

➢ **Hyperbolic process-** A process, in which the gas is heated and expanded in a such a way that the product of its pressure and volume (pv) remains constant, is called a hyperbolic process.

➢ **Adiabatic process (or Isentropic process)-** A process, in which the working substance neither receives nor gives out heat to its surroundings, during its expansion or compression, is called an adiabatic process.

Cont.

➢ **Polytropic process-** A process that allows the interaction of heat between the system and the surrounding throughout the process. It obeys $pv^n = constant$ where n= polytropic index.

2. **Irreversible non-flow processes-** The free expansion process is an irreversible non-flow process.

Adiabatic Process

In an adiabatic or isentropic process, no heat leaves or enters the gas.

Now consider m kg of a certain gas being heated adiabatically from an initial state 1 to a final state 2.

Let P_1, V_1, and T_1— Pressure, volume and temperature at the initial state 1

P_2, V_2, and T_2— Pressure, volume and temperature at the final state 2

The process is shown on the p-v diagram in Fig.

Pressure-volume-temperature (p-v-T) relationship
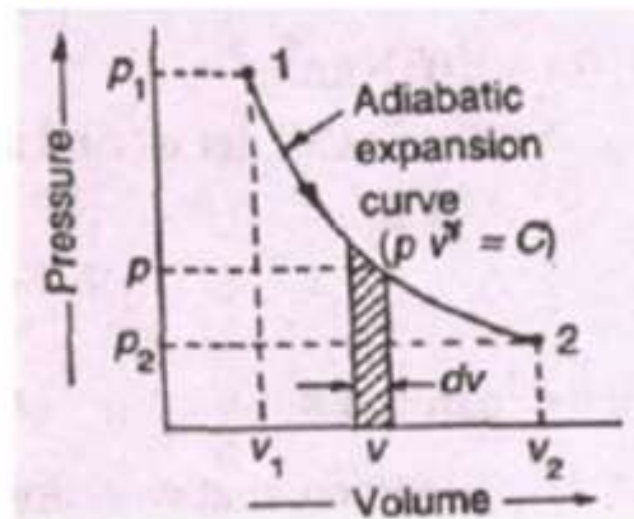
From 1st Law of thermodynamics,

$$\delta Q = \delta W + dU \ldots\ldots\ldots (1)$$

Since no heat transfer takes places, $\delta Q = 0$

$$\therefore \delta W + dU = 0$$

Or,
$$pdv + mC_v dT = 0 \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$\therefore dT = \frac{-pdv}{mC_v} \quad \ldots\ldots\ldots\ldots (3)$$

Cont.

We know,

$$pv = mRT \dots\dots\dots\dots (4)$$

Differentiating the equation (4),

$$pdv + vdp = mRdT$$

$$\therefore dT = \frac{pdv + vdp}{mR} = \frac{pdv + vdp}{m(C_p - C_v)} \dots\dots (5) \qquad [C_p - C_v = R]$$

Equating equations (3) and (5),

$$\frac{-pdv}{mC_v} = \frac{pdv + vdp}{m(C_p - C_v)}$$

$$\frac{C_p - C_v}{C_v} = \frac{pdv + vdp}{-pdv}$$

$$\frac{C_p}{C_v} - 1 = -1 - \frac{vdp}{pdv}$$

$$\frac{C_p}{C_v} = -\left(\frac{v}{dv} \times \frac{dp}{p}\right)$$

$$\therefore \gamma = -\left(\frac{v}{dv} \times \frac{dp}{p}\right)$$

$$\therefore \gamma = -\left(\frac{v}{dv} \times \frac{dp}{p}\right)$$

Cont.

$$or, \quad \gamma \times \frac{dv}{v} = -\frac{dp}{p}$$

$$or, \quad \gamma \times \frac{dv}{v} + \frac{dp}{p} = 0 \quad \ldots\ldots\ldots(6)$$

Integrating the equation (6),

$$\gamma log_e v + log_e p = Constant$$

$$or, \quad log_e pv^\gamma = log_e C$$

$$or, \quad pv^\gamma = C$$

$$\therefore p_1 v_1^\gamma = p_2 v_2^\gamma = \cdots = C$$

Workdone during adiabatic expansion

We know that Workdone,

$$\delta W = pdv$$

On integrating from state 1 and state 2,

$$\int_1^2 \delta W = \int_1^2 pdv$$

$$Or, \quad W_{1-2} = \int_1^2 pdv \quad \ldots\ldots\ldots(7)$$

Cont.

Since adiabatic expansion of the gas follows the law,

$$pv^{\gamma} = p_1 v_1^{\gamma}$$

$$or, p = \frac{p_1 v_1^{\gamma}}{v^{\gamma}}$$

Substituting this value of p in equation (7),

$$W_{1-2} = \int_1^2 pdv$$

$$= \int_1^2 \frac{p_1 v_1^{\gamma}}{v^{\gamma}} dv$$

$$= p_1 v_1^{\gamma} \int_1^2 v^{-\gamma} dv$$

$$= p_1 v_1^{\gamma} \left[\frac{v^{-\gamma+1}}{-\gamma+1} \right]_1^2$$

$$= \frac{p_1 v_1^{\gamma}}{1-\gamma} \left[v_2^{1-\gamma} - v_1^{1-\gamma} \right]$$

Cont.

$$= \frac{p_1 v_1^{\gamma} v_2^{1-\gamma} - p_1 v_1^{\gamma} v_1^{1-\gamma}}{1 - \gamma}$$

$$= \frac{(p_1 v_1^{\gamma}) v_2^{1-\gamma} - p_1 v_1^{\gamma} v_1^{1-\gamma}}{1 - \gamma}$$

$$= \frac{p_2 v_2^{\gamma} v_2^{1-\gamma} - p_1 v_1}{1 - \gamma} \qquad [\because p_1 v_1^{\gamma} = p_2 v_2^{\gamma}]$$

$$= \frac{p_2 v_2 - p_1 v_1}{1 - \gamma}$$

$$\therefore W_{1-2} = \frac{p_1 v_1 - p_2 v_2}{\gamma - 1} \quad [for \; expansion]$$

$$\therefore W_{1-2} = \frac{p_2 v_2 - p_1 v_1}{\gamma - 1} \quad [for \; compression]$$

$$[As \; adiabatic \; index \; (\gamma) \; is \; always \; greater \; than \; 1]$$

This is the equation for workdone during adiabatic expansion and compression of gas.

Polytropic Process

Consider m kg of a certain gas being heated poly tropically from an initial state 1 to a final state 2.

Let P_1, V_1, and T_1— Pressure, volume and temperature at the initial state 1

P_2, V_2, and T_2— Pressure, volume and temperature at the final state 2

The process is shown on the p-v diagram.

The (p-v-T) relations for the polytropic process are

$$p_1 v_1^n = p_2 v_2^n = Constant$$

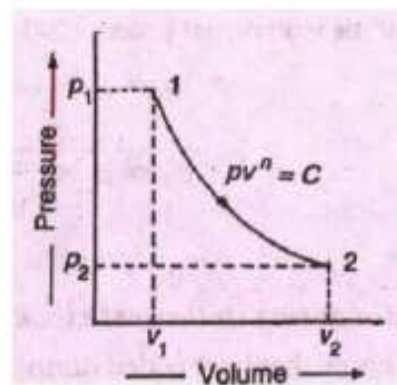$\therefore$ Workdone during a polytropic process from state 1 to state 2,

$$\therefore W_{1-2} = \frac{p_1 v_1 - p_2 v_2}{n-1} \quad [for\ expansion]$$

$$= \frac{mRT_1 - mRT_2}{n-1}$$

$$= \frac{mR(T_1 - T_2)}{n-1}$$

$$\therefore W_{1-2} = \frac{p_2 v_2 - p_1 v_1}{n-1} \quad [for\ Compression]$$

$$= \frac{mR(T_2 - T_1)}{n-1}$$

Cont.

∴ Change in internal energy,

$$dU = U_2 - U_1$$
$$= mC_v(T_2 - T_1)$$

For the case of heat supplied or heat transferred,

$$Q_{1-2} = W_{1-2} + dU$$

$$= \frac{mR(T_1 - T_2)}{n - 1} + mC_v(T_2 - T_1)$$

$$= \frac{mR(T_1 - T_2)}{n - 1} + m \times \frac{R}{\gamma - 1} \times (T_2 - T_1)$$

$$= \frac{mR(T_1 - T_2)}{n - 1} + \frac{mR(T_2 - T_1)}{\gamma - 1}$$

$$= \frac{mR(T_1 - T_2)}{n - 1} - \frac{mR(T_1 - T_2)}{\gamma - 1}$$

$$= mR(T_1 - T_2)\left[\frac{1}{n - 1} - \frac{1}{\gamma - 1}\right]$$

$$= mR(T_1 - T_2)\left[\frac{\gamma - n}{(n - 1)(\gamma - 1)}\right]$$

Cont.

$$= \frac{mR(T_1 - T_2)}{n - 1} \times \frac{\gamma - n}{\gamma - 1}$$

$$= workdone \times \frac{\gamma - n}{\gamma - 1}$$

$$\therefore Q_{1-2} = \frac{\gamma - n}{\gamma - 1} \times workdone$$

Thus heat absorbed or rejected during a polytropic process is $\frac{\gamma - n}{\gamma - 1} \times$ work done.

- **Mathematical Problems-**
  Example: 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 3.10, 3.11, 3.12, 3.13

  -[page- (56-75)]

  A textbook of thermal engineering by R.S. Khurmi

Reference

- A Textbook of Thermal Engineering by R.S. Khurmi and J.K. Gupta (Chapter-1,2, 3, and 4)