First law of thermodynamics

Thermodynamic system:

Definite quantity of matter bounded by some closed surface is known as system. There are mainly three types of systems.

1. **Open system:** If any system can exchange heat energy and mass to its surrounding then such system is known as open system. For example air inside a room.
2. **Closed system:** If any system can exchange only energy but not mass to its surrounding, such system is known as closed system. For example any gas containing in a cylinder having conducting walls is an example of closed system.
3. **Isolated system:** If any system can neither exchange heat energy nor mass with its surrounding such system is known as isolated system. For example any gas containing in a cylinder having perfectly insulating walls so that neither energy nor mass can be exchanged.

Work done by gas

Let us consider a certain mass of gas is filled in a cylinder. P_1,V_1 and T_1 are the initial pressure, volume and temperature of the gas respectively. Let 'dx' is the displacement of the piston due to the force exerted by the gas on it along the direction of force 'F'. If 'A' be the cross-section area of the piston, 'P' be the pressure acting on the piston due to force 'F'.

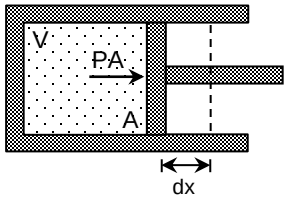

Fig. Work done by a gas during an expansion of dx.

Then,

$$P = \frac{F}{A}$$

$$F = P \times A \ldots\ldots\ldots\ldots \text{(i)}$$

The small work done by gas

$$dW = F \times dx$$

or, $dW = P \times A \times dx$

or, $dW = P \times dV$

If P_2, V_2 and T_2 are the final pressure, volume and temperature of the system, then the total work done by gas W expanding from volume V_1 to V_2 is given by

$$W = \int_{v_1}^{v_2} dW$$

$$\therefore \quad W = P \int_{V_1}^{V_2} dV$$

So, $W = P (V_2 - V_1)$

If work done 'W' is positive, then work is done by gas i.e there is an expansion of gas and if work done 'W' is negative then work is done on gas .

Indicator diagram (P-V diagram)

The graph in which volume is kept along X- axis and pressure is kept along Y- axis is known as indicator diagram or P – V diagram.

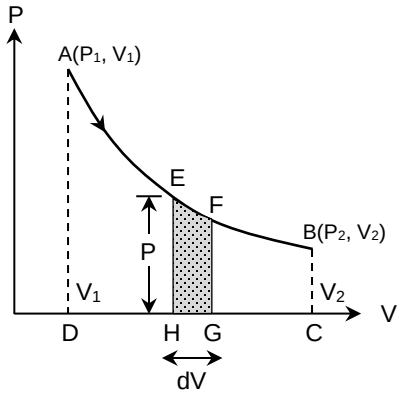

Fig. PV diagram

Let Consider any gas whose pressure and volume at any instant A is (P_1, V_1) and the final pressure and volume at other instant B is (P_2, V_2).

Now, the area of small rectangular strip can be written as,

Area of EFGH= length (EH) × breadth (HG)

= P × dV= small work done by gas.

the total work done is obtained by adding all work done which will be equal to the area enclosed by the curve with the volume axis. Hence area ABCDA gives the total work done of gas.

Work done in a cyclic process.

When a system after passing through different states, returns to its original state, then it is called a cyclic process.

Suppose the gas expands from the initial state A to the final state B along path ACB, as shown in figure.

Then work done by gas is given by

W_1 = + Area ACBB'A'A

Now,

The gas is compressed and is brought to the original state A along the path BDA as shown in figure

Then work done on gas is given by

W_2 = - Area BDAA'B'B

Again,

The network done in the cyclic process is

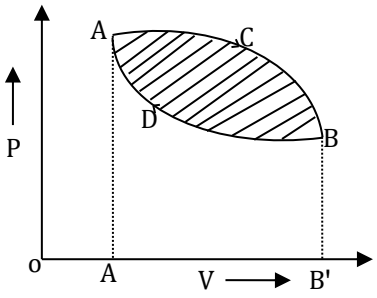

Fig. work done in cyclic process

$W = W_1 + W_2$

= Area ACBB'A'A-Area BDAA'BB

= Area ACBDA

Thus, the net work done on system or by the system in any closed cycle is equal to the area enclosed by the closed loop (shaded area) in PV diagram.

Internal energy of a gas

The sum of kinetic and potential energy of the molecules of a gas is called internal energy of a gas. It is denoted by U and change in internal energy is denoted by dU.

According to Kinetic Theory of gases, the molecules of an ideal gas do not have intermolecular forces between the molecules. Therefore, the molecules of an ideal gas do not possess potential energy due to intermolecular forces and the internal energy of an ideal gas is completely kinetic in nature and is a function of temperature only. But in case of the real gas it possesses intermolecular force between the particles. Hence it possess both Kinetic energy and potential energy. Since kinetic energy is a function of temperature and potential energy is the function of volume, internal energy of a real gas is function of temperature and volume both.

First law of Thermodynamics

The first law of thermodynamics is based on the law of conservation of energy. According to law of conservation of energy, energy can neither be created nor destroyed but it can be changed from one form to another.

According to this law, the total supplied heat to the system may be used partially to increase the internal energy of the system and partially for external work done. If dQ is the heat supplied to the system, dU is the change in internal energy of the system and dW is the small work done at that time. Then from the first law of thermodynamics, we can write

$$dQ = dU + dW$$

or , $dQ = dU + pdV$

Specific Heat Capacity of Gas

Specific heat capacity is defined as the amount of heat required to change the temperature of unit mass or unit mole of gas through unit temperature change.

(i) Principal specific heat capacity at constant volume

It is defined as the amount of heat required to raise the temperature of unit mass of gas through unit temperature difference at constant volume. It is denoted by c_v. Let m is the mass of a gas which is heated by supplying dQ amount of heat through a temperature difference dT keeping its volume constant. Then,

Mathematically, $c_v = \frac{dQ}{mdT}$

(ii) Principal specific heat at constant pressure

It is defined as the amount of heat required to raise the temperature of unit mass of gas by through unit temperature difference at constant pressure. It is denoted by c_p. Let m is the mass of a gas which is heated by supplying dQ amount of heat through a temperature difference dT keeping its pressure constant. Then,

Mathematically, $c_p = \frac{dQ}{mdT}$

(iii) Molar specific heat capacity of gas at constant volume:

It is defined as the amount of heat required to raise the temperature of unit mole of gas by through unit temperature difference at constant volume. It is denoted by C_V. Let n is the total moles of a gas which is heated by supplying dQ amount of heat through a temperature difference dT keeping its volume constant. Then,

Mathematically,

$C_v = \frac{dQ}{ndT}$

(iv) Molar specific heat capacity of gas at constant pressure:

It is defined as the amount of heat required to raise the temperature of unit mole of gas through unit temperature difference at constant pressure. It is denoted by C_p. Let n is the total moles of a gas which is heated by supplying dQ amount of heat through a temperature difference dT keeping its pressure constant. Then,

Mathematically,

$$C_p = \frac{dQ}{ndT}$$

Relation between Two Specific Heat Capacities of Gas (Mayer's Relation)

Consider n-mole of ideal gas is enclosed within a cylindrical vessel having frictionless, airtight and movable piston let P, V and T be the initial pressure, volume and temperature of gas respectively.

Suppose the gas is heated at constant volume and its temperature increase by 'dT' then, amount of heat supplied to the system.

$dQ = n C_v dT$ ……..(i).

Now, From first law of Thermodynamics.

$dQ = dU + PdV$ ……(ii)

at constant volume, $dV = 0$

Then, $dQ = dU$

$\therefore$ $dU = nC_v dT$ ……(iii)

Similarly,

when the gas is heated at constant pressure from same initial condition such that its temperature increase by amount of dT then,

Total amount of heat supplied is given by

$dQ = nC_p dT$ ……(iv) Where C_p = molar specific heat capacity of gas at constant pressure.

Again,

From equation (ii) and (iv)

$nC_p dT = dU + PdV$

Since, internal energy of ideal gas is only function of temperature and independent of volume so,

$nC_p dT = nC_v dT + PdV$ ……..(v)

For n-mole of ideal gas,

$PV = nRT$ ……..(vi)

Differencing both side with respect to Temperature 'T' at constant pressure (P).

We get,

$$\frac{d}{dT}(PV) = \frac{d}{dT}(nRT)$$

$$P\frac{dV}{dT} = nR\frac{dT}{dT}$$

$PdV = nRdT$ …….(vii)

from equation (v) and (vii)

$nC_p dT = nC_v dT + nRdT$

or, $C_p = C_v + R$

$\therefore$ $C_p - C_v = R$ ……(viii) which is required expression and this relation is called Mayer's formula.

If M be the molar mass of the gas then dividing the above equation by 'M' to its both side.

$$\frac{C_P}{M} - \frac{C_V}{M} = \frac{R}{M}$$

Or, $\boxed{c_P - c_V = r}$

Where $\frac{R}{M}$ = r is gas constant per unit mass for a given gas.

Thermodynamic Processes

The continuous change in the state of a given sample of a gas is called thermodynamic process.

1. Isothermal process

The process in which pressure and volume of a system change without changing its temperature is called isothermal process.

For isothermal process to take place,the cylinder should have conducting walls and the gas should be compressed or allowed to expand very slowly.

From First law of Thermodynamics

$dQ = dU + PdV$

or, $dQ = nC_v dT + PdV$ [since change in internal energy is only function of temperature]

at Isothermal process.

$dT = 0$

$\therefore \quad dQ = PdV$

Thus, During Isothermal process, total amount of heat supplied is converted into work done.

In isothermal process, $dU = 0$

$\therefore \quad U = \text{constant}$

i.e.Internal energy remains constant

Work done during Isothermal process

Consider n mole of an ideal gas kept inside a cylinder having conducting base so that process is isothermal. If P, V and T be the pressure, volume and temperature of the gas, let the gas undergoes isothermal process such that its volume change from V_1 to V_2 then,

$$W = \int_{V_1}^{V_2} PdV \quad \ldots\ldots\ldots\ldots\ldots \text{(i)}$$

For n mole of an ideal gas,

$PV = nRT$

$$P = \frac{nRT}{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(ii)}$$

Now, from equation (i) and (ii)

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

R is constant quantity and for isothermal process, temperature is also constant. So,

$$W = nRT \int_{V_1}^{V_2} \frac{1}{V} dx$$

$$W = nRT \, [\log_e V]_{V_1}^{V_2}$$

$$W = nRT \, (\log_e V_2 - \log_e V_1)$$

$$\boxed{W = nRT \log_e \frac{V_2}{V_1}} \quad [\because \log a - \log b = \log \tfrac{a}{b}]$$

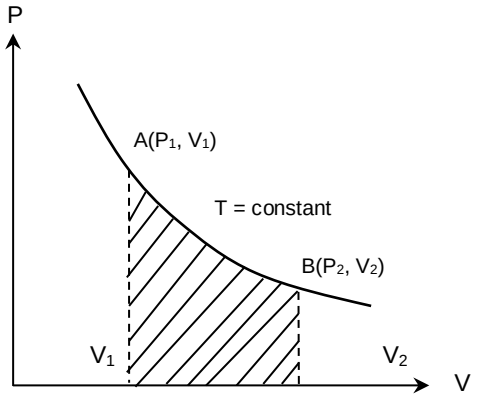

Fig. work done during isothermal process

or, $\boxed{W = 2.303\ nRT \log_{10} \frac{V_2}{V_1}}$

also, for isothermal process,

$P_1V_1 = P_2V_2$

$V_2/V_1 = P_1/P_2$

Then, work done in terms of pressure $\boxed{W = nRT \log_e \frac{P_1}{P_2}}$

or, $\boxed{W = 2.303\ nRT \log_{10} \frac{P_1}{P_2}}$

This is the required expression for the work done during isothermal process.

b. Adiabatic Process:

The process in which pressure, volume and temperature of the system change but there is no exchange of heat between the system and the surroundings is called Adiabatic process.

For adiabatic process to take place,the cylinder should have insulating walls and the gas should be compressed or allowed to expand very quickly.

In this process dQ=0 so from first law

$dU + PdV = 0$

Equation of Adiabatic process

Consider n moles of an ideal gas kept inside cylinder having movable, airtight and frictionless piston in a vessel made of insulating material.

If dQ is the amount of heat supplied to the gas, dU is the change in internal energy of the gas and dW is the small work done by the gas. Then from first law of thermodynamic, we have

$dQ = dU + dW$

or, $dQ = dU + PdV$

But for adiabatic process $dQ = 0$

Then, $dU + PdV = 0$ .....(i)

Since the change in internal energy is the amount of energy which is used by the system to change its temperature only i,e not to change its volume,

$dU = nC_vdT$ ....(ii) ; where, C_v = molar specific heat capacity of gas at constant volume.

From equation (i) and (ii),

$\therefore nC_vdT + PdV = 0$.....(iii)

Also for n mole of an ideal gas, from ideal gas equation,

$PV = nRT$

Differentiating both sides with respect to T, we get,

$PdV + VdP = nRdT$

$dT = \frac{1}{nR}(PdV + VdP)$ ..... (iv)

Substituting value of dT from equation (iv) in (iii), we get,

$\frac{C_V}{R}(PdV + VdP) + PdV = 0$

or, $\frac{C_vPdV + C_vVdP + RPdV}{R} = 0$

or, $C_vPdV + RPdV + C_vVdP = 0$

or, $[C_v + R]\ PdV + C_vVdP = 0$

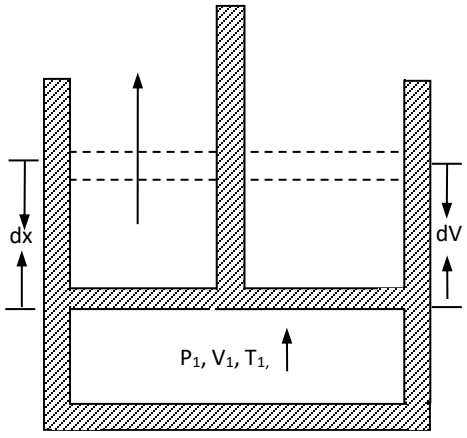

Fig. Derivation of equation of adiabatic process

or, $C_P\, PdV + C_v VdP = 0$.....(iv) [$\because$ $C_p - C_v = R$ so, $C_P = C_v + R$]

Dividing both sides by C_vPV, we get,

$$\frac{C_pPdV}{C_vVP} + \frac{C_vVdP}{C_vVP} = 0.$$

or, $\gamma \frac{dV}{V} + \frac{dP}{P} = 0$; where $\Upsilon = \frac{C_p}{C_V}$ is the ratio of molar specific heat capacities of the gas.

Integrating both sides we get,

$$\gamma \int \frac{dV}{V} + \int \frac{dP}{P} = 0$$

or, $\gamma \log_e V + \log_e P = \text{Constant}$

or, $\log_e V^\gamma + \log_e P = \text{Constant}$

or, $\log_e (V^\gamma P) = \text{Constant}$

Taking antilog on both side, we get

$V^\gamma.P = \text{Constant}$

$\therefore PV^\gamma = \text{Constant}$ ..... (v)

This is the adiabatic equation in terms of pressure and volume.

In general $P_1V_1^\gamma = P_2V_2^\gamma$

Adiabatic equation in terms of temperature and volume.

We have PV = nRT (from ideal gas equation)

or, $P = \frac{nRT}{V}$

Substituting this value of P in equation (v), we get,

$$\frac{nRT}{V} V^\gamma = \text{constant}$$

or, $nRTV^{\gamma-1} = \text{constant}$

$\therefore$ $TV^{\gamma-1} = \text{constant}$

In general $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

Adiabatic equation in terms of temperature and pressure

Substituting $V = \frac{nRT}{P}$ in equation (v), we get

$$P\left(\frac{nRT}{P}\right)^\gamma = \text{constant}$$

or, $P^{1-\gamma} T^\gamma (nR)^\gamma = \text{constant}$

$\therefore$ $P^{1-\gamma}T^\gamma = \text{constant}$

In general $P_1^{1-\gamma}T_1^\gamma = P_2^{1-\gamma}T_2^\gamma$

Work done during an adiabatic Process

Consider n mole of an ideal gas enclosed in a cylinder having perfectly insulated walls and a frictionless piston made of insulating material. Let, it expands adiabatically from an initial volume V_1 to a final volume V_2.The work done by the gas in this process is given by

$$W = \int_{V_1}^{V_2} PdV \text{ .....(i)}$$

Where P is the instantaneous pressure of gas while suffering an infinitesimal expansion dV.

From equation of adiabatic process, $PV^\gamma = K$(Constant)

$$P = \frac{K}{V^\gamma}$$

Therefore, $W = \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV = K \int_{V_1}^{V_2} V^{-\gamma} dV = K\left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_1}^{V_2}$

$$= \frac{K}{1-\gamma} [V_2^{1-\gamma} - V_1^{1-\gamma}]$$

$$= \frac{1}{1-\gamma} [KV_2^{1-\gamma} - KV_1^{1-\gamma}] \text{.....(ii)}$$

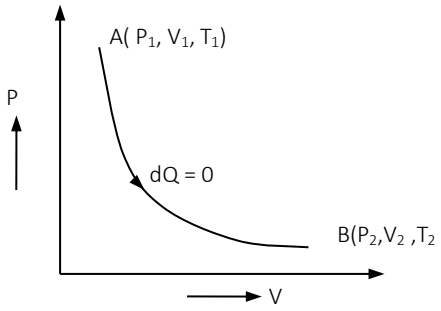

Fig. PV diagram

Now, $P_1V_1^\gamma = P_2^\gamma V_2^\gamma = K$

$\therefore$ $W = \frac{1}{1-\gamma} [P_2V_2^\gamma V_2^{1-\gamma} - P_1V_1^\gamma V_1^{1-\gamma}]$

or, $W = \frac{1}{1-\gamma} [P_2V_2 - P_1V_1]$ ..... (iii)

We know, for n mole ideal gas,

$$P_1V_1 = nRT_1$$

$$P_2V_2 = nRT_2$$

or, $W = \frac{1}{1-\gamma} [nRT_2 - nRT_1]$

or, $W = \frac{nR}{1-\gamma} [T_2 - T_1]$

Since the value of Υ is greater than one,

$$W = \frac{nR}{\gamma - 1} [T_1 - T_2]$$

Hence the work done in adiabatic process depends only upon the initial temperature T_1 and final temperature T_2.

c) Isobaric process:-

The process in which volume and temperature of system change without changing its pressure is called Isobaric process.

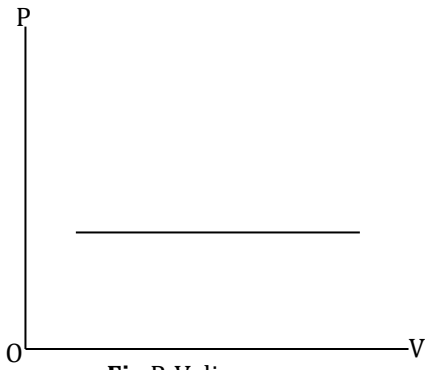

Fig.P-V diagram

d) Isochoric process:

The process in which the pressure and temperature of system change without changing its volume is called Isochoric process.

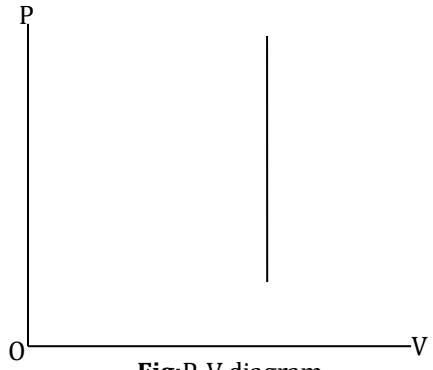

Fig:P-V diagram

wReversible Process

A reversible process is that process which can be retraced in the opposite direction so that the working substance passes through exactly the same condition as it does in the direct process

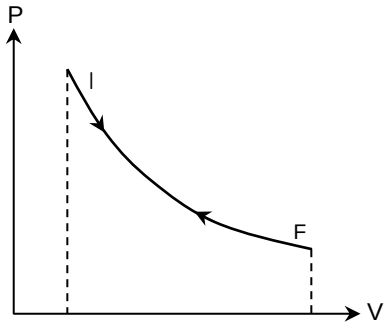

Fig. PV diagram for reversible process

Irreversible Process

An irreversible process is the process which cannot be retraced in the opposite direction when the process is reversed. In nature all processes are irreversible because no natural process can fulfill the stringent requirement of a reversible process.