$$T_4 = T_3\left[\frac{V_3}{V_2}\right]^{\gamma-1}\left[\frac{V_2}{V_1}\right]^{\gamma-1}$$

$$T_4 = T_3[e]^{\gamma-1}\left[\frac{1}{\rho}\right]^{\gamma-1}$$

$$T_4 = T_2[e][e]^{\gamma-1}\left[\frac{1}{\rho}\right]^{\gamma-1}$$

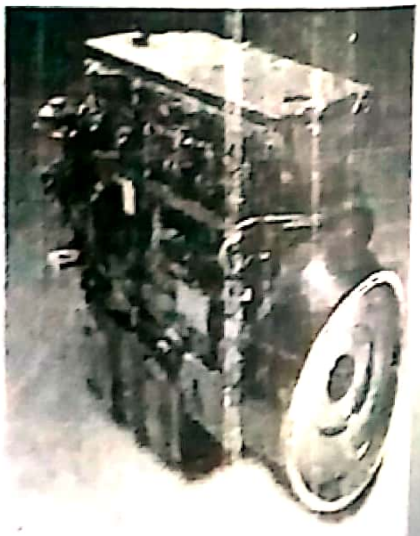
$$T_4 = T_2[e]^{\gamma}\left[\frac{1}{\rho}\right]^{\gamma-1}$$

$$\eta = 1-\left[\frac{T_4-T_1}{T_3-T_2}\right]$$

$$= 1-\frac{1}{\gamma}\left[\frac{T_2[e]^{\gamma}\left[\frac{1}{\rho}\right]^{\gamma-1}-T_3\left[\frac{1}{\rho}\right]^{\gamma-1}}{T_2[e]-T_2}\right]$$

$$\eta = 1-\frac{1}{\gamma}\left(\frac{1}{\rho}\right)^{\gamma-1}\left[\frac{e^{\gamma}-1}{e-1}\right]$$

For the same compression ratio, the efficiency of an Otto engine is more than a diesel engine. In practice the compression ratio for an Otto engine is from 7 to 9 and for a diesel engine it is from 15 to 20. Due to the higher compression ratio, an actual diesel engine has higher efficiency than the Otto (Petrol) engine. The cylinder must be strong enough to withstand very high pressure.



4.34 Multicylinder Engine

With an engine having one cylinder, the engine works only during the working stroke. The piston moves during the rest of the three strokes due to the momentum of the shaft. In a multicylinder engine (say 4-cylinder engine) the four cylinders are coupled. The working of each cylinder is given below:

	First	*Second*	*Third*	*Fourth*
First quarter	Working	Exhaust	Compression	Charging
Second quarter	Exhaust	Charging	Working	Compression
Third quarter	Charging	Compression	Exhaust	Working
Fourth quarter	Compression	Working	Charging	Exhaust

In this way, the power of the engine increases and the shaft gets momentum during each cycle.

Efficiency

From B to C, the pressure remains constant. Considering 1 gram of the working substance, the quantity of heat absorbed,

$$Q_1 = 1 \times C_p (T_3 - T_2)$$

From D to A the volume remains constant.

The quantity of heat rejected,

$$Q_2 = 1 \times C_v (T_4 - T_1)$$

Dividing, we get

$$\frac{Q_2}{Q_1} = \frac{C_v}{C_p} \cdot \frac{(T_4 - T_1)}{(T_3 - T_2)}$$

$$= \frac{1}{\gamma} \cdot \frac{(T_4 - T_1)}{(T_3 - T_2)}$$

Efficiency,

$$\eta = 1 - \frac{Q_2}{Q_1}$$

$$= 1 - \frac{1}{\gamma}\left(\frac{T_4 - T_1}{T_3 - T_2}\right) \qquad ...(4.29)$$

To evaluate $\left(\frac{T_4 - T_1}{T_3 - T_2}\right)$, all the temperatures are to be expressed in terms of T_2.

Let ρ be the adiabatic expansion ratio. Then $\rho = \frac{V_1}{V_2}$ and e the combustion expansion ratio or fuel cut off ratio $= \frac{V_3}{V_2}$.

1. The points A and B are on the same adiabatic,

$$\therefore \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_1 = T_2\left[\frac{V_2}{V_1}\right]^{\gamma-1}$$

$$= T_2\left[\frac{1}{\rho}\right]^{\gamma-1} \qquad ...(4.30)$$

2. The points B and C are at the same pressure

$$\therefore \quad \frac{T_3}{V_3} = \frac{T_2}{V_2}$$

or

$$T_3 = T_2\left[\frac{V_3}{V_2}\right] = T_2[e] \qquad ...(4.31)$$

3. The points C and D are on the same adiabatic.

$$\therefore \quad T_4 V_4^{\gamma-1} = T_3 V_3^{\gamma-1}$$

$$[\text{But } V_4 = V_1]$$

$$T_4 = T_3\left[\frac{V_3}{V_1}\right]^{\gamma-1}$$

$$= T_3\left[\frac{V_3}{V_2} \times \frac{V_2}{V_1}\right]^{\gamma-1}$$

or $$\frac{W}{Q_1'} > \frac{W}{Q_1}$$

or $$Q_1 > Q_1'$$

and $$Q_1' - Q_2' = Q_1 - Q_2$$

or $$Q_2 - Q_2' = Q_1 - Q_1'$$

Now because $$Q_1 > Q_1'$$

$$\therefore \quad Q_2 > Q_2'$$

Now suppose the two engines are coupled together so that I drives R backwards and suppose they use the same source and sink. The combination forms a self-acting machine in which I supplies external work W and R absorbs this amount of work in its reverse cycle. I in its cycle absorbs heat Q_1' from the source and gives up heat Q_2' to the sink. R in its reverse cycle, absorbs heat Q_2 from the sink and gives up heat Q_1 to the source.

The net result of the complete cycle of the coupled engines is given by

Gain of heat by the source at $T_1 = Q_1 - Q_1'$

Loss of heat by the sink at $T_2 = Q_2 - Q_2'$

External work done on the system = 0

Thus, the coupled engines forming a self-acting machine unaided by any external agency transfer heat continuously from a body at low temperature to a body at a higher temperature.

This conclusion is contrary to the second law of thermodynamics, according to which in a cyclic process heat cannot be transferred from one body to another at a higher temperature by a self-acting machine. Hence our assumption is incorrect and we conclude that no engine can be more efficient than a perfectly reversible engine working between the same temperatures.

Second Part: The second part of the theorem may be proved by the same arguments as before. For this purpose, we consider two reversible engines R_1 and R_2 and assume that R_2 is more efficient than R_1. Proceeding in the same way we can show that R_2 cannot be more efficient than R_1. Therefore, all reversible engines working between the same two temperatures have the same efficiency.

Thus, the efficiency of a perfectly reversible engine depends only on the temperatures between which the engine work, and is independent of the nature of the working substance.

4.30 Steam Engine

It consists of a steam chest and a cylinder. These are connected by the steam ports P_1 and P_2. P is a piston that moves inside the cylinder. V is a sliding valve which can also move to and fro such that the port P_1 or P_2 is open to the steam chest. The piston and the sliding valve are connected to the main shaft eccentrically at diametrically opposite points such that when the shaft rotates they move in opposite directions. W is a flywheel attached to the main shaft. The coupling between the main rod and the piston rod is such that the linear motion of the piston rod is converted to circular motion of the shaft. The machinery to be operated is connected to the main shaft.

Working

1. Steam at high pressure from the boiler enters the steam chest. The steam enters the cylinder through the port P_1. The piston P is pushed down due to the high pressure of steam (Fig. 4.19) The sliding valve moves up. Both the ports P_1 and P_2 are closed. This steam inside the cylinder expands and moves the piston further in the downward direction. At this position, the port P_1 is connected to the exhaust valve E and P_2 is opened.

-11

of work i.e. perpetual motion of the second kind is impossible. The engine must reject a part of t heat absorbed to a sink at lower temperature.

These two statements can be combined into one equivalent statement, known as the Kelvi **Planck's statement** of the second law of thermodynamics.

Kelvin-Planck Statement

"It is impossible to construct an engine which, operating in a cycle, has the sole effect of extr ing heat from a reservoir and performing an *equivalent* amount of work."

Clausius's Statement

According to Clausius "It is impossible for a self-acting machine working in a cyclic proc unaided by external agency, to transfer heat from a body at a lower temperature to a body at a hig temperature."

In other words it may be stated as "Heat cannot flow of itself from a colder body to a ho body."

This statement is based upon the performance of refrigerator – a heat engine working in backward direction. This statement means that natural flow of heat is always from a hot body to a c body. If heat is to be transferred from cold body to hot body, work will have to be done by ext agency. A refrigerator is a device which transfers heat from a colder body to hotter body by do external work on the working substance. The compression is brought about by an external agency 'electricity' by performing work on the working substance.

4.29 Carnot's Theorem

Statement

From the second law of thermodynamics two important results are derived; these conclusions are taken together to constitute Carnot's theorem which may be stated in the following forms.

(*a*) 'No engine can be more efficient than a perfectly reversible engine working between the same two temperatures.'

(*b*) 'The efficiency of all reversible engines, working between the same two temperatures is the same, whatever the working substance.'

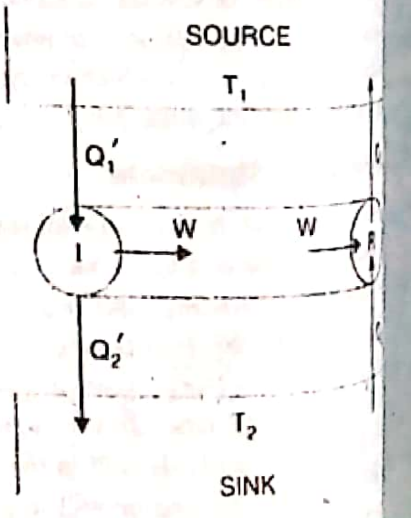


Fig. 4.18

Proof:

First Part: To prove the first part of the theorem, we consider two engines *R* and *I* working between the temperatures T_1 and T_2 where $T_1 > T_2$ [Fig. 4.18]. Of these two engines *R* is reversible and *I* is irreversible.

Suppose *I* is more efficient than *R*. Suppose in each cycle, R absorbs the quantity of he from the source at T_1 and rejects the quantity of heat Q_2 to the sink at T_2. Suppose in each cy absorbs the quantity of heat Q_1' from the source at T_1 and gives up the quantity of heat Q_2' t sink at T_2. Let the two engines do the same amount of work *W* in each cycle. According t assumption *I* is more efficient than *R*.

$$\therefore \quad \frac{Q_1' - Q_2'}{Q_1'} > \frac{Q_1 - Q_2}{Q_1}$$

$$\text{or} \qquad \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

Thus, equation (4.25) can also be expressed as

$$\text{coefficient of performance, } P = \frac{T_2}{T_1 - T_2} \qquad \text{...(4.26)}$$

4.28 Second Law of Thermodynamics

The first law of thermodynamics states the equivalence of heat and energy. It simply tells that whatever work is obtained, an equivalent amount of heat is used up, or vice versa. It does not say anything about the direction in which the change might occur or about the range or limit to which it can be possible. The first law shows that perpetual motion of the first kind is impossible *i.e.* energy can not be created out of nothing or production of energy without disappearance of an equivalent energy of another form is not possible.

The first law has no answer why heat always flows from a body at high temperature to a body at lower temperature and does not flow in the reverse direction. It can not explain why vast amount of available heat connot be converted into mechanical work. If we could control and make use of the limitless store of heat viz-solar energy, we could have an inexhaustible supply of useful energy. Thus, we could have a perpetual motion machine not forbidden by the first law. This is called perpetual motion of the second kind. In practice, however there is no engine which can convert the heat from the single source in to useful work without rejecting some heat to a heat sink at a lower temperature *i.e.* perpetual motion of the second kind *i.e.* production of useful energy from the internal energy of one body is impossible.

It was the quest of several such questions which led to the formulation of second law of thermodynamics. The second law is a generalization of certain experiences and observations and is concerned with the direction in which energy transfer takes place. The law has been stated in a number of ways, which means the same thing.

Lord Kelvin's Statement

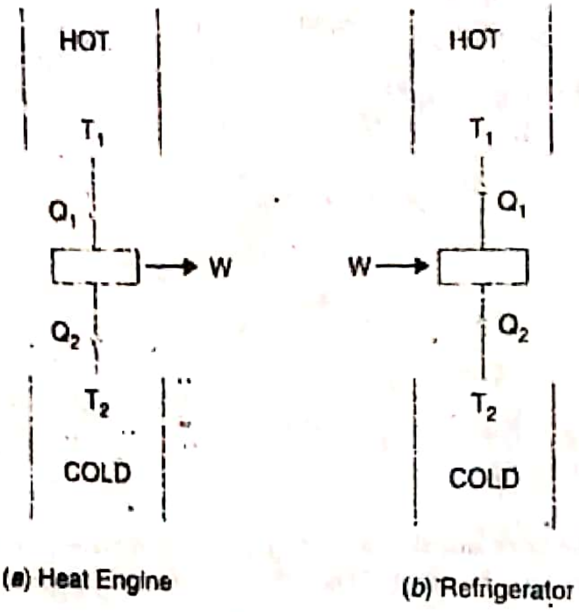
In a heat engine the working substance extracts heat from the source, converts a part of it into work and rejects the rest to a sink at a lower temperature. The temperature of the source must be higher than the surroundings and engine will not work when the temperatures of source and sink are the same. No engine has ever been constructed which converts all the heat absorbed from the source into work without rejecting a part of it to the cold body. As the engine absorbs more and more heat from the hot body, the latter suffers a continuous fall in temperature and if a continuous supply of work is desired, the hot body will in the long run become as cold as its surroundings. Then no heat flow will be possible, the engine will stop working and hence no mechanical work will be obtained. It means that we can not obtain a continuous supply of work from a single supply of it *i.e.* the presence of colder body is a must for the continuous conversion of heat into work. Such considerations led Lord Kelvin to state that

"It is impossible to get a continuous supply of work from a body by cooling it to a temperature lower than that of its surroundings."

Planck's Statement

"It is impossible to construct an engine which, working in a complete cycle, will produce no effect other than the raising of a weight and the cooling of a heat reservoir."

Thus, it is impossible to construct an engine which working in a complete cycle, will produce no effect other than the absorption of heat from a reservoir and its conversion into an equivalent amount



(*a*) Heat Engine (*b*) Refrigerator

Fig. 4.17

When it is operated as a refrigerator, it absorbs heat Q_2 from the sink at temperature T_2. W amount of work is done on it by some external means and rejects heat Q_1 to the source at temperature T_1. ($T_1 > T_2$) as shown in [Fig. 4.17 (*b*)].

In the second case [Fig. 4.17 (*b*)], heat flows from a body at a lower temperature T_2 to a body at a higher temperature T_1 with the help of external work done on the working substance. This action is that of a refrigerator. In every cycle, heat Q_2 is extracted from the cold body. This will not be possible if the cycle is not completely reversible.

4.27 Coefficient of Performance

The amount of heat absorbed at the lower temperature is Q_2. The amount of work done on the working substance by the external agency (input energy) = W and the amount of heat rejected = Q_1. Here Q_2 is the desired refrigerating effect in each cycle.

$$\therefore \text{ Coefficient of performance, } P = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} \qquad \text{...(4.25)}$$

Suppose 200 joules of energy is absorbed at the lower temperature and 100 joules of work is done on it by external help. Then, 200 + 100 = 300 joules are rejected at the higher temperature.

The coefficient of performance

$$P = \frac{Q_2}{W}$$

$$= \frac{Q_2}{Q_1 - Q_2}$$

$$= \frac{200}{300 - 200} = 2$$

Therefore, the coefficient of performance of a refrigerator is 200%.

In the case of heat engine, the efficiency cannot be more than 100% but in case of a refrigerator, the coefficient of performance can be much higher than 100%.

If the working substance is an ideal gas, then

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_1 - Q_2}{T_1 - T_2}$$

Efficiency,
$$\eta = \frac{\text{Useful Output}}{\text{Input}} = \frac{W}{Q_1}$$
$$= \frac{(Q_1 - Q_2)}{Q_1}$$
$$= \frac{R(T_1 - T_2)\log_e \frac{V_2}{V_1}}{RT_1 \log_e \frac{V_2}{V_1}}$$
$$\eta = \frac{T_1 - T_2}{T_1} \quad \text{...(4.23)}$$

or
$$\eta = 1 - \frac{T_2}{T_1} \quad \text{...(4.24)}$$

From equation (4.24), we conclude that the efficiency depends only upon the temperature of the source and sink and is always less than unity. The efficiency is independent of the nature of working substance. From equation, $\eta = 1 - \frac{T_2}{T_1}$, we get $\eta = 1$, if T_2 = 0K *i.e.* the temperature of the sink is at absolute zero degrees. In practice, it is never possible to reach absolute zero and hence 100% conversion of heat energy into mechanical work is not possible.

Again, the efficiency is minimum or zero when $T_1 = T_2$ *i.e.* the temperature of the source is equal to the temperature of sink, then $\eta = 0$ *i.e.* the engine does not work.

The Carnot's heat engine is perfectly reversible. It can be operated in the reverse direction also. Then it works as a refrigerator. The heat Q_2 is taken from the sink and external work is done on the working substance and heat Q_1 is rejected to the source at a higher temperature (principle of a refrigerator).

Moreover in the Carnot's heat engine, the process of isothermal and adiabatic expansions and compressions are carried out very-very slowly *i.e.* quasi-static. This is an ideal case. Any practical engine can not satisfy these conditions. Therefore, all practical engines have an efficiency less than the Carnot's engine.

4.25 Effective Way to Increase Efficiency

The expression for the efficiency of a Carnot's engine is
$$\eta = 1 - \frac{T_2}{T_1}$$

The efficiency η can be increased by one of the following ways.

(*i*) Using a heat-source at constant temperature T_1 and heat-sink at temperature as low as possible, or

(*ii*) Using a heat-sink at constant temperature T_2 and a heat-source at temperature as high as possible.

In practice, it is not convenient to use heat sink at a temperature below that of the atmosphere. Therefore, the more effective way to increase the efficiency is to use a heat-source at temperature as high as possible.

4.26 Carnot's Engine and Refrigerator

Carnot's cycle is perfectly reversible. It can work as a heat engine and also as a refrigerator. When it is operated as a heat engine, it absorbs heat Q_1 from the source at a temperature T_1, does an amount of work W and rejects heat Q_2 to the sink at temperature T_2, ($T_2 < T_1$) as shown in [Fig. 4.17 (*a*)]

Work done by the engine per cycle

During the above cycle, the working substance absorbs an amount of heat Q_1 from the source and rejects Q_2 to the sink.

Hence, the net amount of heat absorbed by the gas per cycle

$$= Q_1 - Q_2$$

The net work done by the engine per cycle

$$= W_1 + W_2 + W_3 + W_4$$

$$= W_1 + W_3 \qquad (\because W_2 = -W_4$$

From the graph, the net work done per cycle

$$= \text{area } ABGEA + \text{area } BCHGB - \text{area } CHFDC - \text{area } DFEA$$

$$= \text{area } ABCDA$$

Thus, the area enclosed by the Carnot's cycle consisting of two isothermals and two adiabatic gives the net amount of work done per cycle.

In the cyclic process,

$$\text{Net heat absorbed} = \text{Net work done per cycle.}$$

$$Q_1 - Q_2 = W_1 + W_3$$

$$= RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_3}{V_4} \qquad \text{...(4.1}$$

Since the points A and D lie on the same adiabatic DA

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \qquad \text{...(4.2}$$

Similarly, points B and C lie on the same adiabatic BC

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\therefore \qquad \frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \qquad \text{...(4.2}$$

From equations (5.20) and (5.21),

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

or

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}$$

or

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Substituting in equation (5.19), we get

$$\text{Net work done} = Q_1 - Q_2 = RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_2}{V_1}$$

$$W = (Q_1 - Q_2) = R(T_1 - T_2) \log_e \frac{V_2}{V_1} \qquad \text{...(4.}$$

Efficiency

The efficiency of the heat engine is the rate of quantity of heat converted into work (U output) per cycle to the total amount of heat absorbed per cycle

This operation is represented by the adiabatic BC, starting from the state $B\,(P_2, V_2, T_1)$ to the state $C\,(P_3, V_3, T_2)$. In this process, there is no transfer of heat, the temperature of the substance falls to T_2 and it does some external work W_2 given by

$$W_2 = \int_{V_2}^{V_3} P.dV = K\int_{V_2}^{V_3} \frac{dV}{V^\gamma}$$

(∵ During adiabatic process, PV^γ = constant = K)

$$= \frac{KV_3^{1-\gamma} - KV_2^{1-\gamma}}{1-\gamma}$$

$$= \frac{P_3V_3 - P_2V_2}{1-\gamma} \qquad (\because P_2V_2^\gamma = P_3V_3^\gamma = K)$$

$$= \frac{RT_2 - RT_1}{1-\gamma}$$

$$= \frac{R(T_1 - T_2)}{\gamma - 1} = \text{Area } BCHGB \qquad \text{...(4.16)}$$

3. **Isothermal Compression.** The cylinder is now removed from the insulating stand and is placed on the sink which is at a temperature T_2. The piston is now very slowly moved inwards so that the work is done on the gas. The temperature tends to increase due to heat produced by compression since the conducting base of the cylinder is in contact with the sink, the heat developed passes to the sink and the temperature of the gas remains constant at T_2. Thus the gas undergoes isothermal compression at a constant temperature T_2 and gives up some heat to the sink.

This operation is represented by the isothermal CD, starting from the state $C\,(P_3, V_3, T_2)$ to the state $D\,(P_4, V_4, T_2)$. In this process, the substance rejects heat Q_2 to the sink at T_2 and work W_3 is done on the substance given by

$$Q_2 = W_3 = \int_{V_3}^{V_4} PdV = RT_2 \log_e \frac{V_4}{V_3} \qquad \text{...(4.17)}$$

$$= -RT_2 \log_e \frac{V_3}{V_4} = \text{area } CHFDC$$

(– *ve* signe indicates that work is done on the working substance)

4. **Adiabatic Compression.** The cylinder is now removed from sink and again placed on the insulating stand. The piston is slowly moved inwards so that the gas is adiabatically compressed and the temperature rises. The adiabatic compression is continued till the gas comes back to its original condition *i.e.* state $A\,(P_1, V_1, T_1)$, thus completing one full cycle.

This operation is represented by adiabatic DA, starting from $D\,(P_4, V_4, T_2)$ to the final state $A\,(P_1, V_1, T_1)$. In this process, work W_4 is done on the substance and is given by

$$W_4 = \int_{V_4}^{V_1} P.dV$$

$$= -\frac{R(T_1 - T_2)}{\gamma - 1} = \text{Area } DFEAD \qquad \text{...(4.18)}$$

(– *ve* sign idicates that work is done on the working substance. Since W_2 and W_4 are equal and opposite, they cancel each other.)

2. **Source.** A reservoir maintained at a constant temperature T_1 from which the engine ca draw heat by perfect conduction. It has infinite thermal capacity and any amount of heat can be dra from it at constant temperature T_1.

3. **Heat insulating stand.** A perfectly non-conducting platform acts as a stand for adiaba processes.

4. **Sink.** A reservoir maintained at a constant lower temperature T_2 ($T_2 < T_1$) to which the he engine can reject any amount of heat. The thermal capacity of sink is infinite so that its tempera remains constant at T_2, no matter how much heat is given to it.

4.24 Carnot's Cycle

In order to obtain a continuous supply of work, the working substance is subjected to the follo ing cycle of quasi-static operations known as Carnot's cycle (Fig. 4.16).

1. **Isothermal expansion.** The cylinder is first placed on the source, so that the gas acqu the temperature T_1 of the source. It is then allowed to undergo quasi-static expansion. As the g expands, its temperature tends to fall. Heat passes into the cylinder through the perfectly cond base which is in contact with the source. The gas therefore, undergoes slow isothermal expans the constant temperature T_1.

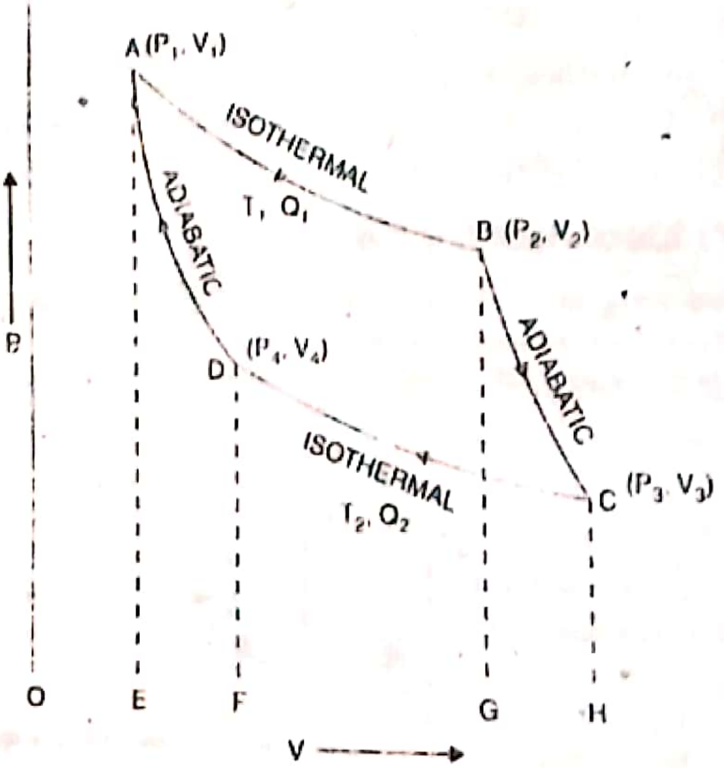


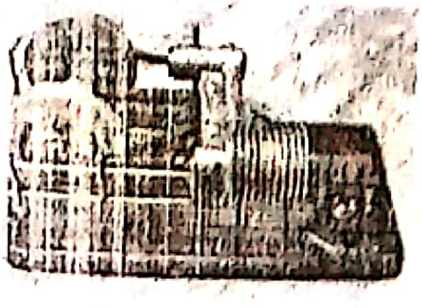
Fig. 4.16

Let the working substance during isothermal expansion goes from its initial state A (P_1, V_1, T_1 the state B (P_2, V_2, T_1) at constant temperature T_1 along AB. In this process, the substance absorbs Q_1 from the source at T_1 and does work W_1 given by

$$Q_1 = W_1 = \int_{V_1}^{V_2} PdV = RT_1 \log_e \frac{V_2}{V_1} = \text{area } ABGEA$$

2. **Adiabatic expansion.** The cylinder is now removed from the source and is placed o insulating stand. The gas is allowed to undergo slow adiabatic expansion, performing external at the expense of its internal energy, until its temperature falls to T_2, the same as that of the sin

4.21 Heat Engines



Heat Engine

Any practical machine which converts heat into mechanical work is called a heat engine. Heat engines in their operation absorb heat at a higher temperature, converts part of it into mechanical work, and rejects the remaining heat at a low temperature. In this process, a working substance is used. In steam engines, the working substance is water vapour, and in all gas engines the working substance is a combustible mixture of gases.

In any heat engine, the working substance goes through certain changes of pressure, volume and temperature, and then returns to the initial state. The complete changes through which the working substance undergoes from its initial state and back to its starting state constitute one cycle of operation.

4.22 Definition of Efficiency

The efficiency, η, of a heat engine is defined as the ratio of the mechanical work done by the engine in one cycle to the heat absorbed from the high temperature source. Thus

$$\eta = \frac{Q_1 - Q_2}{Q_1} \qquad \ldots(4.14)$$

where Q_1 is the heat absorbed from the source at high temperature, Q_2, is the heat rejected to a sink at low temperature and $(Q_1 - Q_2)$ is the mechanical work done by the engine in one cycle.

Since $(Q_1 - Q_2) < Q_1$, the efficiency can never be 100%.

4.23 Carnot's Ideal Heat Engine

In 1824 the French engineer Sadi Carnot conceived a theoretical engine which is free from all practical imperfections. Such an engine can not be realised in practice. It has maximum efficiency and it is an ideal heat engine. Sadi Cornot's heat engine requires the following important parts (Fig. 4.15):

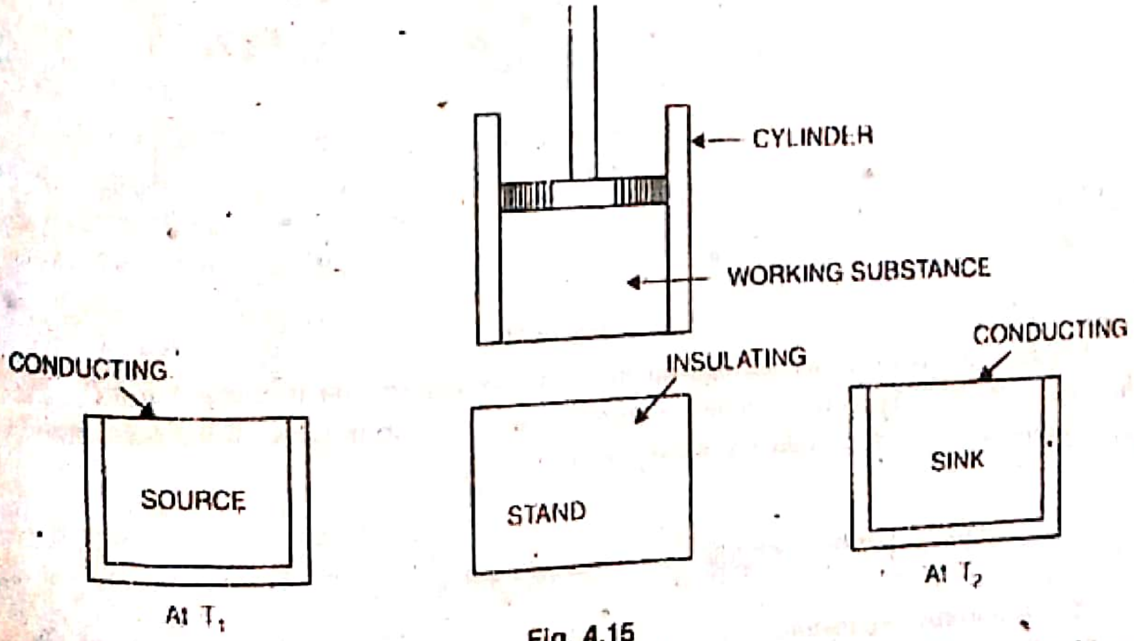


Fig. 4.15

1. **A cylinder** having perfectly non-conducting walls, a perfectly conducting base and is provided with a perfectly non-conducting piston which moves without friction in the cylinder. The cylinder contains one mole of perfect gas as the working substance.

4.20 Reversible and Irreversible Process

Reversible Process

A reversible process is one which can be retracted in opposite direction by changing the external conditions infinitesimally.

The working substance in the reverse process passes through all the stages as in the direct process in such a way that all changes occurring in the direct process are exactly repeated in the opposite order and inverse sense and no changes are left in any of the bodies participating in the process or in the surroundings. If heat is absorbed by the substance in the direct process, the same quantity of heat will be given out by it in the reverse process, and if work is done by the substance in the direct process, an equal amount of work will be done on the substance in the reverse process. Thus, there is no wastage or loss of energy at all in the reversible process.

Consider a gas enclosed in a cylinder, made of a perfectly conducting material and immersed in a large tank of water of a constant temperature. Suppose the gas is compressed very slowly such that its temperature remains unchanged throughout. Obviously to do so, small pauses will have to be given in between various small compressions to enable the heat generated by compression to pass out in to the surrounding water. If now after reducing considerably the volume of the gas, it is now allowed to expand isothermally and the expansion be just as infinitely small as done in compression with similar pauses in between, heat will flow in from enclosing water and the temperature of the gas remains unchanged. Exactly the same amount of heat will be received during the expansion as was given up during compression. Thus, all the stages of the direct process are retracked in the opposite direction and inverse order. Hence the infinitesimally slow isothermal expansion and compression of a gas is a reversible process. Infact **all isothermal and adiabatic operations are reversible when carried out very slowly.**

The process will not be reversible if there is any loss of heat due to friction, radiation or conduction. If the changes take place rapidly, the process will not be reversibly. The energy used in over coming friction can not be retraced.

The conditions of reversibility for any heat engine or process can be stated as follows.

1. The pressure and temperature of the working substance must not differ appreciably from those of the surrounding at any stage of the cycle of operation.
2. All the processes taking place in the cycle of operation must be infinitely slow.
3. The working parts of the engine must be completely free from friction.
4. There should not be any loss of energy due to conduction, convection or radiation during the cycle of operation.

It should be remembered that the complete reversible process or cycle of operation is only an ideal case. In an actual process, there is always loss of heat due to friction, conduction, convection or radiation.

Irreversible Process

In nature all changes are irreversible because of the following reasons : (1) The conditions for thermodynamic equilibrium *i.e.* mechanical, thermal or chemical equilibrium are not satisfied because a natural process does not take place quasi-statically. (2) Dissipative effects, such as friction, viscosity, inelasticity, electric resistance, eddy formation etc. are always present.

Examples of some natural irreversible processes are, spontaneous expansion of a gas into an evacuated space, spontaneous conduction of heat along a metal bar which is hot at one end and cold at the other, transfer of heat by radiation from a hotter to a colder body, transfer of electricity through a resistor. Nonetheless reversible processes are most important in thermodynamics because they can be handled analytically.

$$\therefore \quad \frac{d^2y}{dt^2} + \frac{\gamma PA^2}{VM} \cdot y = 0 \qquad \text{...}(ii)$$

Equation (*ii*) represents S.H.M.

Let the time period be t

$$t = 2\pi\sqrt{\frac{\text{displacement}}{\text{acceleration}}}$$

$$= 2\pi\sqrt{\frac{y}{-d^2y/dt^2}}$$

$$t = 2\pi\sqrt{\frac{VM}{\gamma PA^2}}$$

$$\gamma = \frac{4\pi^2 VM}{PA^2t^2} \qquad \text{...}(iii)$$

As V, M, P and A are already known, only the time period t is to be determined.

Hence γ can be calculated.

This experiment is not very accurate because the ball comes to rest in a short time due to friction and the time period cannot be determined accurately.

Rinkle's Modification

Rinkle suggested a modification in Ruchhardt's experiment. The ball is kept in the equilibrium position where the pressure of air (or gas) is exactly equal to the atmospheric pressure. The ball is allowed to drop and the distance L through which it drops before starting to move up again is noted. This distance is found accurately by taking a series of photographs of the moving ball.

$$\text{Work done} = \int_0^L F\,dy$$

But

$$F = \frac{\gamma P_0A^2y}{V}$$

$$W = \frac{\gamma P_0A^2}{V}\int_0^L y\,dy$$

$$= \frac{\gamma P_0A^2L^2}{2V} \qquad \text{...}(iv)$$

$$\text{Work done} = MgL \qquad \text{...}(v)$$

Equating (*iv*) and (*v*)

$$\frac{\gamma P_0A^2L^2}{2V} = MgL$$

$$\gamma = \frac{2MgV}{P_0A^2L} \qquad \text{...}(vi)$$

As M, g, V, P_0 and A are known, L is measured from the photographic film. Hence γ can be calculated. The error in the result is due to the following assumptions: (*i*) that there is no friction, (*ii*) that the gas is ideal and (*iii*) the process is completely adiabatic.

$$\left(\frac{P_1}{P_0}\right)^{\gamma-1} = \left(\frac{T_1}{T_0}\right)^{\gamma}$$

$$(\gamma-1)(\log P_1 - \log P_0) = \gamma[\log T_1 - \log T_0]$$

$$\gamma = \frac{\log P_1 - \log P_0}{(\log P_1 - \log P_0) - (\log T_1 - \log T_0)}$$

As P_1, P_0, T_1 and T_0 are known, γ can be calculated. The value of γ for air at 17°C is found to be 1.4034.

Advantages.

1. Due to the large volume of the vessel, the expansion is adiabatic.
2. The temperatures are measured accurately just before and after the adiabatic expansion.

Drawbacks.

This method cannot be used to find the value of γ at higher temperatures because it is not possible to determine the cooling correction accurately.

4.19 Ruchhardt's Experiment

In 1929, Ruchhardt designed an apparatus to find the value of γ. It is based on the principle of mechanics. Air (or gas) is enclosed in a big jar (Fig. 4.14). A tube of uniform area of cross section is fitted and a ball of mass m fits in the tube just like a piston. In the equilibrium position, the ball is at the point A. The pressure P of air inside the vessel, is given by

$$P = P_0 + \frac{mg}{A}$$

where P_0 is the atmospheric pressure and A is the area of cross-section of the tube.

The ball is given a small downward movement through a distance y. It moves up and down and executes simple harmonic motion. Let the change in volume be dV and change in pressure be dP.

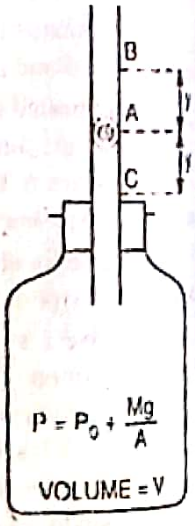


Fig. 4.14

$$dV = yA$$

and $$dP = \frac{F}{A}$$

where F is the restoring force

As the ball moves quite rapidly, the process of change in P and V is adiabatic.

$$\therefore \qquad PV^{\gamma} = \text{const}$$

Differentiating, $P\gamma V^{\gamma-1}\,dV + V^{\gamma}.\,dP = 0$

$$\gamma P dV + V dP = 0$$

Substituting the values of dV and dP,

$$\gamma PyA + \frac{V.F}{A} = 0$$

But $$F = M\frac{d^2y}{dt^2}$$

or $$F = -\frac{\gamma PA^2}{V}\,y \qquad \text{...(i)}$$

Approximately,
$$\gamma = \frac{\frac{H}{P_0}}{\frac{H-h}{P_0}} = \frac{H}{H-h}$$

Hence
$$\gamma = \frac{H}{H-h} \qquad \ldots (iv)$$

Similarly, γ for any gas can be determined by this method.

Drawbacks

When the stop-cock is opened, a series of oscillations are set up. This is shown by the up and down movement of the liquid in the manometer. Therefore, the exact moment when the stopcock should be closed is not known. The pressure may not be equal to the atmospheric pressure when the stop-cock is closed. It may be higher or less than the atmospheric pressure. Thus the result obtained will not be accurate.

4.18 Partington's Method

Lummer, Pringsheim and Partington designed an apparatus to determine the value of γ. In this method, the pressure and temperature are measured accurately before and after the adiabatic expansion.

The apparatus consists of a vessel A having a capacity between 130 and 150 litres. The valve L can be opened and closed suddenly.

It is controlled by a spring arrangement (Fig. 4.13). Dry air (or gas) at a pressure higher than the atmospheric pressure is forced into the vessel A and the stop-cock S is closed. The oil manometer M is used to measure the pressure of air inside the vessel A. The bolometer B (a platinum wire) and a sensitive galvanometer are used in the Wheatstone's bridge arrangement.

The vessel is surrounded by a constant temperature bath. Let the initial pressure and temperature be P_1 and T_1 (room temperature). The bridge is kept slightly disturbed from the balanced position.

The valve L is suddenly opened and closed. The Wheatstone's bridge is at once adjusted for balanced position. The temperature of air inside A has decreased due to adiabatic expansion of air. Let the temperature inside be T_0 and the atmospheric pressure P_0. If the apparatus is allowed to remain as such for some time, it will gain heat from the surroundings and the balance point gets disturbed. In order that the balance point remains undisturbed, some pieces of ice are added into the water surrounding the vessel A. When the temperature of water bath is the same as that of air just after adiabatic expansion, the bridge will remain balanced.

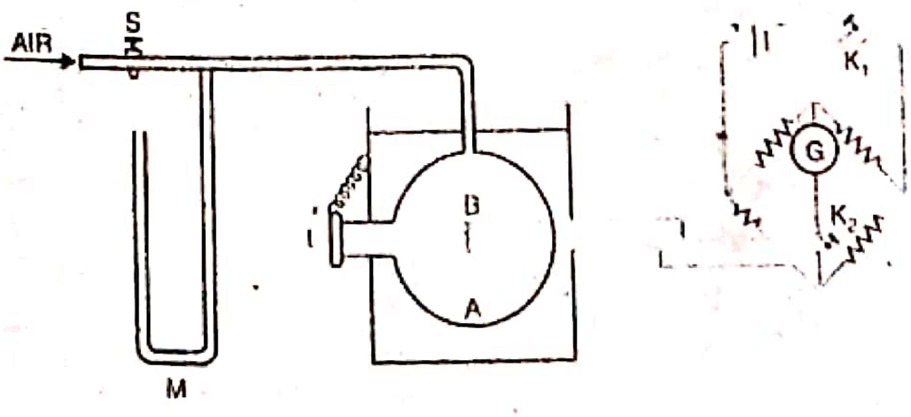


Fig 4.13

The temperature T_0 of the bath represents the temperature of air after the adiabatic expansion.

$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_0^{\gamma-1}}{T_0^{\gamma}}$$

The stop-cock S is suddenly opened and closed just at the moment when the levels of the on the two sides of the manometer are the same. Some quantity of air escapes to the atmospher air inside the vessel expands adiabatically. The temperature of air inside the vessel falls due to batic expansion. The air inside the vessel is allowed to gain heat from the surroundings and it attains the temperature of the surroundings. Let the pressure at the end be P_2 and the differe levels on the two sides of the manometer be h.

Theory

Consider a fixed mass of air left in the vessel in the end. This mass of air has expanded from volume V_1 (less than the volume of the vessel) at pressure P_1 to volume V_2 at pressure P_0. The process is adiabatic as shown by the curve AB (Fig. 4.12).

$$P_1 V_1^{\gamma} = P_0 V_2^{\gamma}$$

$$\frac{P_1}{P_0} = \left(\frac{V_2}{V_1}\right)^{\gamma} \qquad ...(i)$$

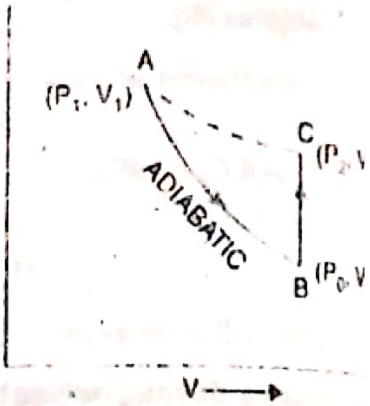


Fig. 4.12

Finally the point C is reached. The points A and C are at the room temperature. Therefore AC can be considered as an isothermal.

$$P_1 V_1 = P_2 V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

Substituting the value of $\frac{V_2}{V_1}$ in equation (i),

$$\frac{P_1}{P_0} = \left(\frac{P_1}{P_2}\right)^{\gamma}$$

Taking logarithms,

$$\log P_1 - \log P_0 = \gamma [\log P_1 - \log P_2]$$

$$\gamma = \frac{\log P_1 - \log P_0}{\log P_1 - \log P_2}$$

But

$$P_1 = P_0 + H \text{ and } P_2 = P_0 + h$$

∴

$$\gamma = \frac{\log(P_0 + H) - \log P_0}{\log(P_0 + H) - \log(P_0 + h)}$$

$$\gamma = \frac{\log\left(\frac{P_0 + H}{P_0}\right)}{\log\left(\frac{P_0 + H}{P_0 + h}\right)}$$

$$= \frac{\log\left(1 + \frac{H}{P_0}\right)}{\log\left(1 + \frac{H - h}{P_0 + h}\right)}$$

Substituting in eqn. (v), the change in temperature

$$dT = \frac{-T}{C_F}\left(\frac{\partial l}{\partial T}\right)_F dF \qquad ...(viii)$$

Since length increasess with increase in temperature, $\left(\frac{\partial l}{\partial T}\right)$ is positive, from eqn (*viii*), therefore, we conclude that wire of those substances which expand on heating, show a cooling effect when stretched adiabatically.

If β is coefficient of linear expansion, m the mass per unit length, then $\beta = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_F$ or

$\left(\frac{\partial l}{\partial T}\right)_F = \beta l$ and $C_F = mlC_P$

$$\therefore \qquad dT = -\frac{T}{mlC_P}\beta l d_F = \frac{-T\beta}{mC_P} dF \qquad ...(ix)$$

This gives fall in temperature due to adiabatic stretching of a wire.

3. Adiabatic demagnetisation of paramagnetic salt

In this case, $X = -H$ and $x = I$

Substituting in eqn. (v), the change in temperature

$$dT = -\frac{T}{C_H}\left(\frac{\partial I}{\partial T}\right)_H dH \qquad ...(x)$$

where C_H is the specific heat of the substance at constant field.

Here $\left(\frac{\partial I}{\partial T}\right)_H$ is always negative. Hence R.H.S. is always positive. If H decreases, dH is – *ve* and hence dT is –*ve*. Hence, a cooling is produced during adiabatic demagnetisation of a paramagnetic substance.

4.17 Clement and Desormes Method-Determination of γ

Clement and Desormes in 1819 designed an experiment to find γ, the ratio between the two specific heats of a gas.

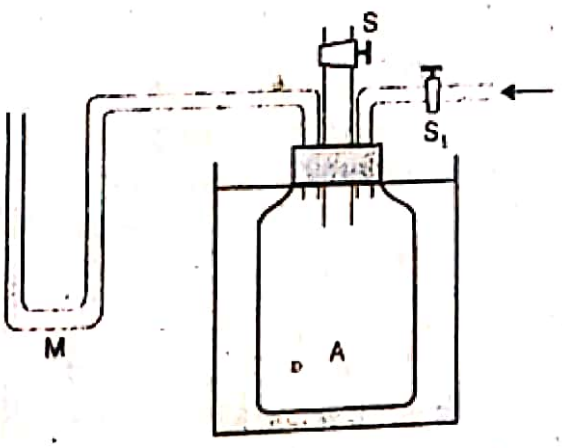


Fig. 4.11

The vessel A has a capacity of 20 to 30 litres and is fitted in a box containing cotton and wool. At the top end, three tubes are fitted as shown in Fig. 4.11. Through S_1, dry air is forced into the vessel A. The stop cock S_1 is closed when the pressure inside A is slightly greater than the atmospheric pressure. Let the difference in level on the two sides of the manometer be H and the atmospheric pressure be P_0. The pressure of air inside the vessel is P_1.

At constant pressure, differenting w.r. to T, we get

$$P\left(\frac{\partial V}{\partial T}\right)_P = nR$$

Multiplying both sides by T, we get

$$PT\left(\frac{\partial V}{\partial T}\right)_P = nRT = PV$$

or $$T\left(\frac{\partial V}{\partial T}\right)_P = V$$

Substituting for V in eqn. (*iii*), we have

$$PdV = -\frac{T}{\gamma}\left(\frac{\partial V}{\partial T}\right)_P dP$$

Substituting for PdV in eqn. (*ii*), we get

$$dT = \frac{T}{\gamma C_V}\left(\frac{\partial V}{\partial T}\right)_P dP$$

But $$\gamma = \frac{C_P}{C_V} \quad \text{or} \quad \gamma C_V = C_P$$

$$\therefore \quad dT = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{...}(iv)$$

In terms of generalised coordinates, the change in temperature during adiabatic process may be written as

$$dT = \frac{T}{C_X}\left(\frac{\partial x}{\partial T}\right)_X dx \qquad \text{...}(v)$$

This is the equation of state of the system in terms of generalised parameters. Substituting the corresponding values of parameters, the change in temperature of the system undergoing adiabatic process can be evaluated. Let us examine the same for the three cases:

1. Adiabatic expansion of gas

In case of a gas

$$X = P \quad \text{and} \quad x = V$$

substituting in eqn. (*v*), the change

$$dT = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{...}(vi)$$

During expansion, dP decreases *i.e.* falls. It means the temperature of the gas also decreases. Thus, if a highly campressed gas is suddenly allowed to expand adiabatically, the gas cools considerably.

If α is the coefficient of volume expansion, given by $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, then

$$dT = \frac{TV\alpha}{C_P} dP \qquad \text{...}(vii)$$

2. Stretching of a wire

3. **Paramagnetic salt :** A system of paramagnetic salt is a function of the magnetic field (H), the intensity of magnetisation (I) and the temperature of the salt (T). *i.e.*, $f(H, I, T)$.

In all these cases, we can calculate the work done (dW) in a reversible infinitesimal change *i.e.*, the corresponding changes in above parameters. Let us write down the work done in each case.

1. In gas expansion the work done by the system is

$$dW = P \, . dV$$

2. In stretching a wire, the work done is

$$dW = -F \, . dl$$

3. The paramagnetic salt in a magnetic field,

$$dW = -H \, dI$$

We presume here that the work done by the system is positive. For example: in case of gas expansion, the gas does work against a pressure, in stretching a wire, the work is done by tension F to produce a change in length through dl, because the wire by iteself wants to contract due to its elasticity and not to expand, as is the case in a gas. Hence -ve sign is used with Fdl. The same is true for the case of a paramagnetic salt in magnetic field, *i.e.*, $dW = -HdI$.

A general formula, which will describe the above three systems can be of the form

$$dW = X \, dx \qquad \text{...(i)}$$

where X is called as generalised force and dx as generalised extension. The generalised force ($P, -F, -H$) is a unique function of the extensions (V, l, I) respectively, at a fixed temperature. The generalised parameters for each case will be

1. for Gas expansion, $X = P$ and $dx = dV$
2. for Stretching a wire, $X = -F$ and $dx = dl$
3. for paramagnetic salt in field, $X = -H$ and $dx = dI$

From the first law of thermodynamics

$$\delta Q = dU + \delta W$$

In adiabatic process, $\delta Q = 0$

$$\therefore \qquad dU = -\delta W$$

In terms of generalised parameters

$$dU = -X \, dx$$

But in adiabatic process,

$$dU = C_v \, dT$$

$$\therefore \qquad C_v \, dT = -X \, dx$$

$$\text{or} \qquad dT = -\frac{1}{C_v} X \, dx \qquad \text{...(ii)}$$

In adiabatic process, P and V are related by

$$PV^{\gamma} = \text{constant}$$

Differentiating, we get

$$PV^{\gamma-1} \, dV + V^{\gamma} \, dP = 0 \qquad \text{...(iii)}$$

$$\text{or} \qquad PdV = -\frac{V}{\gamma} dP$$

for n gm. moles of a gas, the equation of state is

$$PV = nRT$$

4.15 Relation Between Adiabatic and Isothermal Elasticities

1. Isothermal Elasticity

During an isothermal process

$$PV = \text{constant}$$

Differentiating,

$$PdV + VdP = 0$$

or

$$\frac{V\,dP}{-dV} = P \qquad \text{...}(i)$$

From the definition of elasticity of a gas

$$E_{iso} = \frac{dP}{-dV/V}$$

$$= \frac{VdP}{-dV} \qquad \text{...}(ii)$$

From (*i*) and (*ii*)

$$E_{iso} = P \qquad \text{...}(iii)$$

2. Adiabatic Elasticity

During an adiabatic process

$$PV^{\gamma} = \text{constant}$$

Differentiating, $P\gamma V^{\gamma-1}\,dV + V^{\gamma}\,dP = 0$

or

$$\frac{VdP}{-dV} = \gamma P \qquad \text{...}(iv)$$

From the definition of elasticity of a gas

$$E_{adi} = \frac{dP}{dV/V}$$

$$= \frac{V\,dP}{-dV} \qquad \text{...}(v)$$

From (*iv*) and (*v*),

$$E_{adi} = \gamma P \qquad \text{...}(vi)$$

Comparing (*iii*) and (*vi*)

$$E_{adi} = \gamma E_{iso}$$

Thus, the adiabatic elasticity of a gas is γ times the isothermal elasticity.

4.16 Cooling Due to Adiabatic Reversible Processes

On the basis of first law of thermodynamics, we can show that when a thermodynamic system such as a gas, stretched wire or a paramagnetic salt is made to undergo an adiabatic process reversibly, the temperature of the system changes. The thermodynamic coordinates taking part in the above three processes are discussed below.

1. **Gas expansion:** A system of gas is a function of three parameters, the pressure (P), the volume (V) and the temperature (T), *i.e.*, $f(P, V, T)$.

2. **Stretched wire:** System of stretched wire is a function of stretching force (F), the length of the stretching wire (l) and the temperature of the wire (T), *i.e.*, $f(F, l, T)$. Here pressure and volume are considered to be constant.

Since A and B lie on the same adiabatic,

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$$

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

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

$$W = \frac{1}{1-\gamma}[P_2V_2 - P_1V_1] \qquad \text{...(4.10)}$$

Taking T_1 and T_2 as the temperatures at points A and B respectively and considering one gram molecule of the gas

$$P_1V_1 = RT_1$$

$$P_2V = RT_2$$

Substituting these values in equation (4.10)

$$W = \frac{1}{1-\gamma}[RT_2 - RT_1]$$

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

$$= \frac{R}{\gamma-1}[T_1 - T_2] \qquad \text{...(4.11)}$$

Hence the work done in adiabatic process depends only upon the initial and final temperatures T_1 and T_2. Thus, *the work done along any adiabatic between two isothermals is independent of the particular adiabatic*.

4.14 Slopes of Adiabatics and Isothermals

In an isothermal process

$$PV = \text{constant}$$

Differentiating

$$P\,dV + V\,dP = 0$$

or

$$\frac{dP}{dV} = -\frac{P}{V} \qquad \text{...(4.12)}$$

In an adiabatic process

$$PV^{\gamma} = \text{constant}$$

Differentiating,

$$P\gamma V^{\gamma-1}\,dV + V^{\gamma}\,dP = 0$$

$$\frac{dP}{dV} = -\frac{\gamma P}{V} \qquad \text{...(4.13)}$$

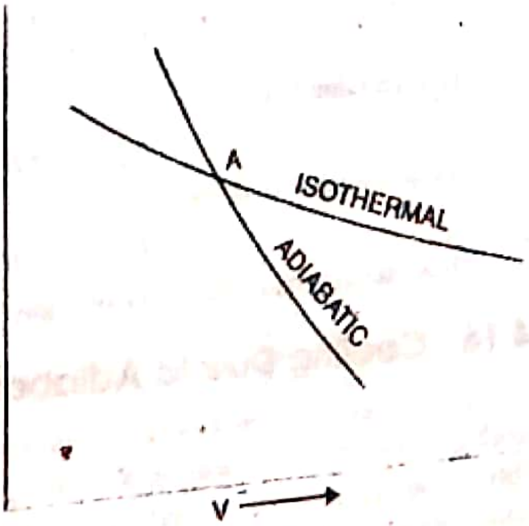


Fig. 4.10

Therefore, the slope $\left(\frac{dP}{dV}\right)$ of an adiabatic is γ

thermal curve (Fig 4.10) at a point A where

Let the initial and final volumes be V_1 and V_2 respectively. Fig 4.8 represents the indicator diagram. The area of the shaded strip represents the work done for a small change in volume dV. When the volume changes from V_1 to V_2

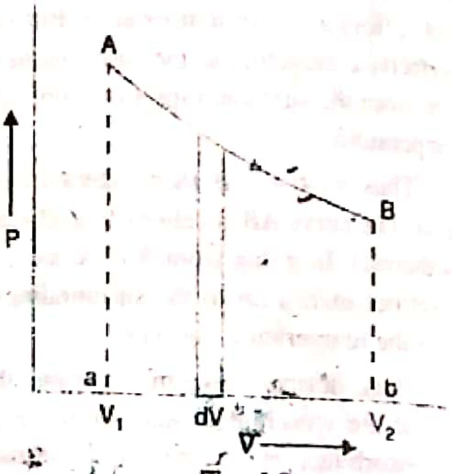


Fig. 4.8

$$\text{Work done} = \int_{V_1}^{V_2} P\,dV = \text{area } ABba$$

Considering one gram molecule of the gas

$$PV = RT$$

or
$$P = \frac{RT}{V}$$

$$\therefore \quad W = RT\int_{V_1}^{V_2}\frac{dV}{V}$$

$$W = RT \times 2.303 \log_{10}\frac{V_2}{V_1} \qquad ...(4.8)$$

Also
$$P_1V_1 = P_2V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\therefore \quad W = RT \times 2.303 \log_{10}\frac{P_1}{P_2} \qquad ...(4.9)$$

Here, the change in the internal energy of the system is zero (because the temperature remains constant). So the heat absorbed by the system is equal to the work done by it.

4.13 Work done During an Adiabatic Process

During an adiabatic process, the system is thermally insulated from the surroundings. The gas expands from volume V_1 to V_2 as shown by indicator diagram [Fig. 4.9]. The work done by the gas for an increase in volume dV is $P\,dV$.

Work done when the gas expands from V_1 to V_2 is given by

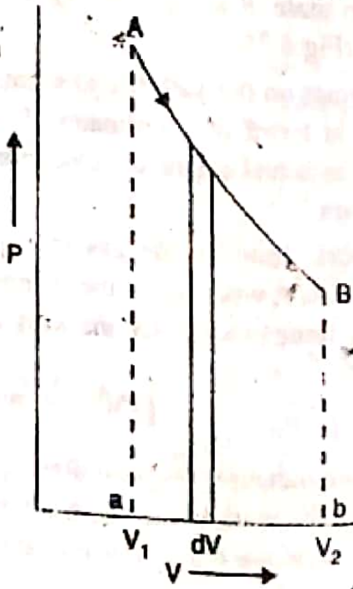


Fig. 4.9

$$W = \int_{V_1}^{V_2} P\,dV = \text{Area } ABba$$

During an adiabatic process

$$PV^{\gamma} = \text{constant} = K$$

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

$$\therefore \quad W = K\int_{V_1}^{V_2}\frac{dV}{V^{\gamma}}$$

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

$$\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_1}$$

Pressure is decreased and work is done by the working substance at the cost of its internal energy and suffers a fall in temperature. But the system is perfectly conducting to the surroundings. It absorbs heat from the surroundings and maintains a constant temperature.

Thus, from A to B, the temperature remains constant. The curve AB is called the isothermal curve or isothermal. In going from B to A back, the system gives out extra heat to the surroundings and maintains the temperature constant.

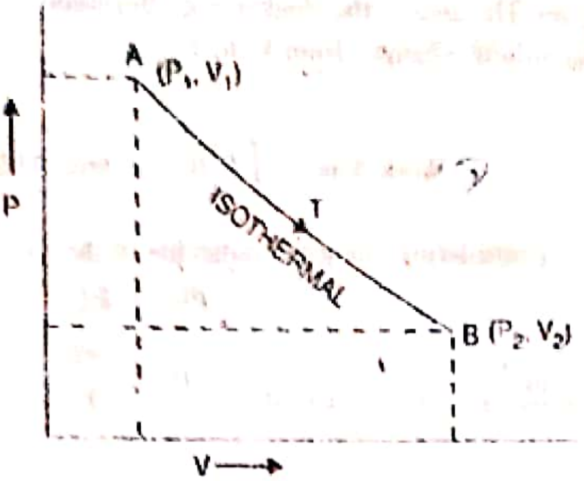


Fig. 4.6

Thus, during isothermal process, the temperature of the working substance remains constant. It can absorb heat or give heat to the surroundings. The equation for isothermal process is

$$PV = RT = \text{constant (for one gram molecule of a gas)}$$

For n gram molecules of a gas,

$$PV = nRT$$

For an ideal gas undergoing isothermal process,

$$(U_2 - U_1) = 0$$

$\therefore$ From the first law of thermodynamics, we get

$$Q = W$$

i.e. in an isothermal process the heat supplied to an ideal gas is equal to the work done by the gas.

4.11 · The Indicator Diagram

It is very convenient to represent the behaviour of an engine by an indicator diagram. This helps to understand the performance of heat engines. Suppose that a system is taken from an initial equilibrium state A to the final equilibrium state B along path AB and the process is quasistatic (Fig 4.7).

Each point on the path traced represents the state of the system in terms of coordinates (P, V). Such a trace obtained in an actual engine is called indicator diagram or $P - V$ diagram.

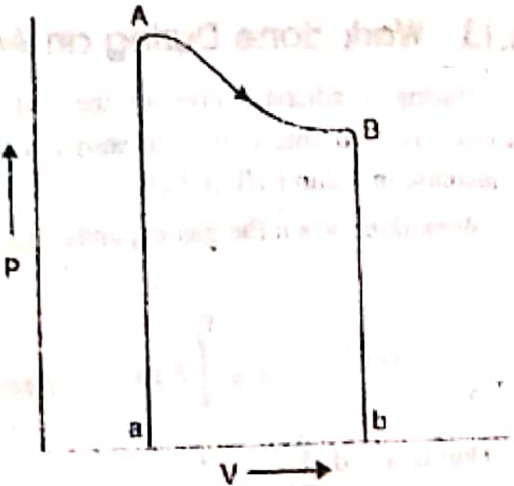


Fig. 4.7

The work done by the gas in expanding against pressure P is PdV, where dV is the infinitesimal change in volume. For finite process AB, the work done

$$= \int PdV = \text{area } ABba$$

Thus, the indicator diagram directly indicates the work done by the engine during each cycle of operation, the work being equal to the area enclosed by the indicator diagram. The work done is +ve if the indicator diagram is traced in clock-wise direction and –ve if the direction is anticlock wise.

Thus, during an adiabatic process

(i) PV^{γ} = constant

(ii) $TV^{\gamma-1}$ = constant, and

(iii) $\dfrac{P^{\gamma-1}}{T^{\gamma}}$ = constant

4.10.5 Cyclic process

For the cyclic process, the law can be stated as

$$\oint dQ = \oint dU + \oint dW$$

In a cyclic process, the system is restored to the initial state at the end of the cycle.

Since, the internal energy is a state function,

$$\therefore \quad \oint dU = 0$$

or $$\oint dQ = \oint dW$$

$\therefore$ Total work obtained = Net Heat supplied

Thus, no work is obtained if no heat is supplied or work can be obtained only at the cost of energy. From indicator diagram (Fig. 4.5), we write

$$Q = \text{Area } ACBDA$$

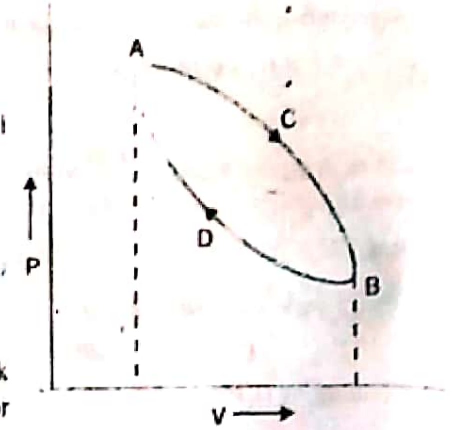


Fig. 4.5

4.10.6 Non-isolated system (Internal energy of the Universe)

System and surroundings together constitutes the universe. In a non-isolated system, heat transfer between the system and the surroundings is allowed. When a heat δQ is supplied to the system its internal energy increases by dU and it performs an external work δW.

$$dQ = dU + \delta W$$

or $$dU = \delta Q - \delta W$$

This gives the change in internal energy of the system.

Here δQ is +ve, since heat enters the system.

δW is +ve, since work is done by the system.

On applying the first law of thermodynamic to the surroundings, which loses a heat δQ and receives a work δW i.e. a work δW is done on the surroundings; hence both δQ and δW are negative for the surroundings.

$\therefore$ Change in internal energy of the surroundings

$$dU' = -\delta Q - (-\delta W)$$

$$dU' = \delta W - \delta Q \qquad \text{...(4.7)}$$

Net change in internal energy $= dU + dU'$

$$= (\delta Q - \delta W) + (\delta W - \delta Q)$$

$$= 0$$

Thus, the net change in internal energy is always zero.

4.10.7 Isothermal process

If a system is perfectly conducting to the surroundings and the temperature remains constant throughout the process, it is called an isothermal process. Consider a working substance at a certain pressure and temperature and having volume represented by the point A (Fig. 4.6).

For an ideal gas of 1 gram, we have

$$PV = rT \qquad \text{...(iii)}$$

where r is ordinary gas constant.

Differentiating,

$$PdV + VdP = rdT$$

Substituting the value of dT in equation (*ii*),

$$C_v\left[\frac{PdV + VdP}{r}\right] + \frac{PdV}{J} = 0$$

$$C_v[PdV + VdP] + r\frac{PdV}{J} = 0$$

But, $$\frac{r}{J} = C_p - C_v$$

$$\therefore \quad C_vPdV + C_vVdP + C_pPdV - C_vPdV = 0$$

$$C_pPdV + C_vVdP = 0$$

Dividing by C_vPV,

$$\frac{C_p}{C_v}\frac{dV}{V} + \frac{dP}{P} = 0$$

But $$\frac{C_p}{C_v} = \gamma$$

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

Integrating, $\log P + \gamma \log V =$ constant

$$\log PV^\gamma = \text{constant}$$

or $$\boxed{PV^\gamma = \text{constant}} \qquad \text{...(iv)}$$

This is the equation connecting pressure and volume during an adiabatic process and is known as *Poisson's law*.

Taking $$PV = rT$$

or $$P = \frac{rT}{V}$$

$$\left(\frac{rT}{V}\right).V^\gamma = \text{constant}$$

But r is constant

$$rTV^{\gamma-1} = \text{constant}$$

$$\therefore \quad TV^{\gamma-1} = \text{constant} \qquad \text{...(v)}$$

Also $$V = \frac{rT}{P}$$

$$P\left[\frac{rT}{P}\right]^\gamma = \text{constant}$$

or $$\frac{r^\gamma T^\gamma}{P^{\gamma-1}} = \text{constant}$$

or $$\frac{P^{\gamma-1}}{T^\gamma} = \text{constant} \quad \text{or} \quad \boxed{TP^{(1-\gamma)/\gamma} = \text{constant}} \qquad \text{...(vi)}$$

4.10.3 Isobaric process (i.e. pressure constant)

If a system undergoes a change in which the pressure is kept constant, the process is called isobaric. Suppose Q is the heat absorbed by a system at constant pressure and suppose its volume increases from V_1 to V_2. Then from the first law, we have

$$Q = (U_2 - U_1) + W$$

or
$$Q = (U_2 - U_1) + P(V_2 - V_1)$$

or
$$Q = (U_2 + PV_2) - (U_1 + PV_1)$$
$$= H_2 - H_1 \quad ...(4.6)$$

where
$$H = U + PV.$$

From equation (4.6), we conclude that the heat absorbed at constant pressure is equal to increase in quantity H, called as *enthalpy*. Like the internal energy U, the quantity H is a function of thermodynamic variables. The quantity H is also called the heat function at constant pressure.

4.10.4 Adiabatic process

When a system undergoes from an initial state to a final state in such a way that no heat leaves or enters the system, the process is called adiabatic. In this process.

$$Q = \boxed{0}$$

∴
$$U_2 - U_1 = -W$$

For an ideal gas
$$U_2 - U_1 = C_V d_T$$

∴
$$W = -C_V d_T$$

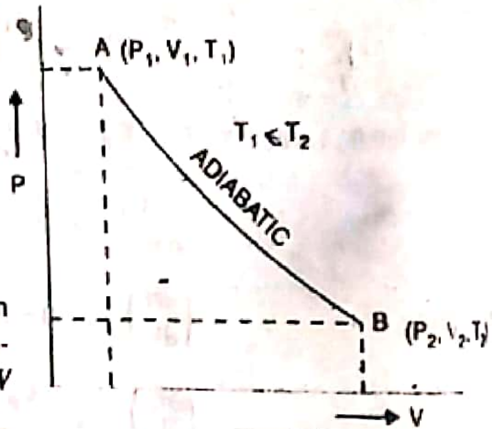


Fig. 4.4

Here W is the work done by the system. Thus, when a system expands adiabatically, its internal energy decreases. If the system is compressed adiabatically then W is negative. Thus, in case of compression

$$U_2 - U_1 = -(-W) = W$$

Therefore, in an adiabatic compression of a system its internal energy increases.

The processes that take place suddenly or quickly are adiabatic processes.

Adiabatic Equation of a Perfect Gas.

Consider 1 gram of the working substance (ideal gas) perfectly insulated from the surroundin Let the external work done by the gas be δW.

Applying the first law of thermodynamics

$$\delta Q = dU + \delta W$$

But
$$\delta Q = 0$$

and
$$\delta W = P.dV$$

where P is the pressure of the gas and dV is the change in volume.

∴
$$0 = dU + \frac{P.dV}{J}$$

where J is mechanical equivalent of heat.

As the external work is done by the gas at the cost of its internal energy, there is fall in tempe ture by dT.

$$dU = 1 \times C_v \times dT \qquad (\because m =$$

$$C'_v dT + \frac{P.dV}{J} = 0$$

For a Reversible Adiabatic Process:

We write, $\delta Q = 0$

Therefore, from equation (*ix*)

$$0 = C_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

or

$$C_V dT = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

Dividing throughout by dV,

$$C_V\left(\frac{\partial T}{\partial V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \qquad \text{...(xii)}$$

The isobaric volume coefficient of expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad \alpha V = \left(\frac{\partial V}{\partial T}\right)_P$$

We have

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad \frac{C_P - C_V}{\alpha V} = P$$

But

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 = P - P$$

or

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{C_P - C_V}{\alpha V}\right) - P \qquad \text{...(xiii)}$$

or

$$-\left(\frac{C_P - C_V}{\alpha V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \qquad \text{...(xiv)}$$

From equation (*xii*) and (*xiv*),

$$C_V\left(\frac{\partial T}{\partial V}\right) = -\left(\frac{C_P - C_V}{\alpha V}\right)$$

or

$$\left(\frac{\partial T}{\partial V}\right) = \frac{C_V - C_P}{\alpha V C_V} \qquad (4.5)$$

This expression holds good for an adiabatic reversible process.

4.10.2 Isochoric process (*i.e.* Volume constant)

If a system undergoes a change in which the volume remains constant, the process is called isochoric. At constant volume, no external work is done *i.e.* $\delta W = 0$

$\therefore$ Heat absorbed is given by $\delta Q = dU$

This expression may be used to define the internal energy of a system

Thus, the increase in the internal energy of a system is equal to the heat absorbed by the system at constant volume. The work done in isochoric process is zero.

and

$$\frac{dV}{dT} = 0$$

$$\therefore \quad \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \qquad \text{...(v)}$$

when the gas is heated at constant pressure,

$$\left(\frac{\delta Q}{dT}\right) = C_P$$

∴ from equation (*iv*)

$$C_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

or

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{...(vi)}$$

From Joule's experiment, for an ideal gas on opening the stopcock, no work was done and no heat transfer took place. So $\delta Q = 0 = dU + 0$. Therefore, $dU = 0$. Even though the volume changed while the temperature is constant, there is no change in the internal energy.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

From the ideal gas equation

$$PV = RT$$

or

$$P\left(\frac{\partial V}{\partial T}\right)_P = R \qquad \text{...(vii)}$$

$$\therefore \quad C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

But

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\therefore \quad C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = R$$

$$\therefore \quad C_P - C_V = R \qquad \text{...(viii)}$$

This formula is known as Mayer's relation.

Here C_P, C_V and R are expressed in the same unit. From equation (*iii*),

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \qquad \text{...(ii)}$$

For a process at constant temperature

$$dT = 0$$

$$\therefore \quad (\delta Q)_T = P(dV)_T + \left(\frac{\partial U}{\partial V}\right)_T (dV)_T \qquad \text{...(ix)}$$

This equation represents the amount of heat energy supplied to a system in an isothermal reversible process and is equal to the sum of the work done by the system and increase in its internal energy

Specific heat at constant volume (C_V) : It is defined as the amount of heat required to raise the temperature of unit mass of a gas through 1 °C, when its volume is kept constant. It is represented by C_V and is given by

$$C_V = \left(\frac{\Delta Q}{\Delta T}\right)_V \qquad \ldots(vi)$$

C_P is greater than C_V : Heat capacity of a gas is different under these two conditions. Suppose the heat is supplied to a gas and is allowed to expand at constant pressure. Then, the heat supplied is used up in doing two things:

(*i*) it raises the temperature of the gas (*i.e.* increase in its internal energy) and

(*ii*) it does work in expanding the gas against the external pressure.

$$\delta Q = dU + \delta W$$
$$= dU + PdV$$

On the other hand, when gas is heated at constant volume, no work is done ($\delta W = P.dV = 0$) and hence whole of the heat supplied is used to raise its temperature. Thus, more heat is required for increasing the temperature of the gas through 1 °C at constant pressure than at constant volume. Hence specific heat of a gas at constant pressure (C_P) is greater than the specific heat at constant volume (C_V); *i.e.*, $C_P > C_V$.

4.10 Applications of First Law of Thermodynamics

4.10.1 Specific Heat of a Gas (*V* and *T* independent)

The internal energy of a system is a single valued function of the state variables viz. pressure, volume, temperature etc. In the case of gas, any two of the variables *P, V, T* are sufficient to define completely its state. If *V* and *T* are chosen as the independent variables,

$$U = f(V, T) \qquad \ldots(i)$$

Differentiating equation (*i*)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \ldots(ii)$$

If an amount of heat δQ is supplied to a thermodynamical system, say an ideal gas and if the volume increases by dV at a constant pressure P, then according to the first law of thermodynamics

$$\delta Q = dU + \delta W$$

Here $\qquad \delta W = P.dV$

$\therefore \qquad \delta Q = dU + P.dV$

Substituting the value of dU from equation (*ii*),

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV \qquad \ldots(iii)$$

Dividing both sides by dT,

$$\frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT} + \frac{PdV}{dT}$$

or
$$\left(\frac{\delta Q}{dT}\right) = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\frac{dV}{dT} \qquad \ldots(iv)$$

If the gas is heated at constant volume,

$$\left(\frac{\delta Q}{\partial T}\right)_V = C_V$$

In other words, the internal energy is a function of any two of the thermodynamic variables P, V and T.

Thus, $U = f(P, V)$ or $U = f(V, T)$ or $U = f(T, P)$

Hence, the differential

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV \qquad \text{...(4.4}$$

is a perfect differential of the thermodynamic variables P and V. Internal energy is an extensiv variable.

4.9 Specific Heats of a Gas

Heat capacity : Different materials have different capacity to absorb heat to produce a giv change of temperature in a given mass. If a material of mass m absorbs heat Q, so that its temperatu rises through ΔT, then

$$\text{Heat capacity} = \frac{Q}{\Delta T} \qquad \text{...(}$$

Specific heat (C) : Heat capacity per unit mass is known as specific heat and is denoted by C

$$\therefore \qquad \text{Specific heat} = \frac{\text{Heat capacity}}{\text{mass}}$$

$$C = \frac{Q}{m.\Delta T} \qquad \text{...(i}$$

Definition : The specific heat of a material is defined as the quantity of heat required to raise th temperature of unit mass of the material through 1 degree.

The unit in C.G.S. is calories per gram per °C. In S.I. it is Joule per kg per °C. For example

$$\text{Specific heat of water} = 1 \text{ cal/gm °C}$$

$$= 1 \text{ Kilo calories/kg °C.}$$

$$= 4.18 \times 10^3 \text{ Joule/kg °C}$$

This definition is sufficient for solids and liquids. Since, the gases are compressible, the speci heat of a gas may vary from 0 to infinity. For examples, if a gas is compressed, it's temperature ris without supplying any heat to it *i.e.* $Q = 0$. Hence, specific heat

$$C = \frac{Q}{m.\Delta T} = 0 \qquad \text{...(}$$

On the contrary, if the gas is allowed to expand freely, without any rise in temperature $(\Delta T =$ then

$$C = \frac{Q}{m \times 0} = \infty \qquad \text{...(}$$

Hence specific heat of a gas is defined by considering any one of the two (either pressure volume) as constant. Thus, a gas has two specific heats:

(*i*) C_P, the specific heat at constant pressure, and

(*ii*) C_V, the specific heat at constant volume.

Specific heat at constant pressure (C_P) : It is defined as the amount of heat required to raise temperature of unit mass of a gas through 1 °C, when its pressure is kept constant. It is represented C_P, and is given by

$$C_P = \left(\frac{\Delta Q}{\Delta T}\right)_P$$

For a very small change in the state of the system, the law is expressed in the differential form a

$$\delta Q = dU + \delta W \qquad ...(4.$$

where δQ and δW are not perfect differentials but dU is a perfect differential because U is a functio of the state of the system.

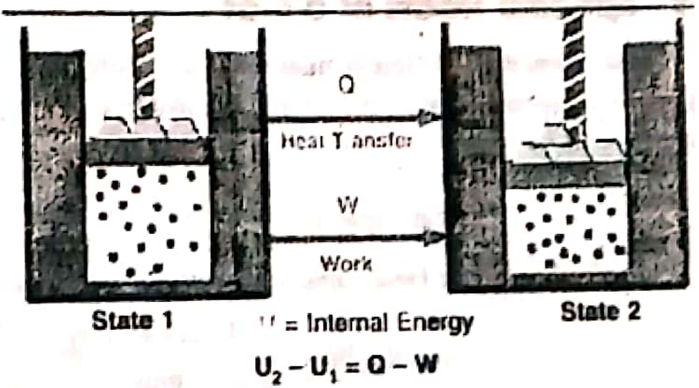
It should be remembered that all the quantities in equation (4.2) or (4.3) must be expressed i unit of energy. The amount of heat Q or δQ is taken positive if heat is supplied to the system, an negative if heat is removed from it. Similarly, the work W or δW is positive when the external work done by the system in expansion and negative if the work is done on it in compression.

Significance of the First Law;

The first law of thermodynamics is important because

- (*i*) it is applicable to any process th which a system undergoes a physical or chemical change.
- (*ii*) it introduces the concept of th internal energy, and
- (*iii*) it provides method for determining the change in the internal energy.

First Law of Thermodynamics



Any thermodynamic system in an equilibrium state possesses state variable called the internal energy (U). Between any two equilibrium states, the change in interna energy is equal to the difference of the heat transfer into the system and work done by the system.

Limitations of the First Law:

The first law of thermodynamics is based on the principle of conservation of energy of a system. Though it is applicable to every process in nature between the equilibrium states, it does not specify the condition under which a system can use its heat energy produce a supply of mechanical work. It also does not say how much of the heat energy can converted into work.

4.8 Internal Energy as a State Function

forming a system and W is the work d

2. Starting from point A the volume V_1 is kept constant in going from A to D, the pressure decreases from P_1 to P_2 and then P_2 is kept constant from D to B. The work done in this process *i.e.* along ADB path given by

$$W_2 = P_2(V_2 - V_1) = \text{area } DBFE$$

3. Again starting from point A, the pressure P_1 is kept constant in going from A to C and the the volume V_2 is kept constant from C to B. The work done in this process *i.e.* along path ACB is give by

$$W_3 = P_1(V_2 - V_1) = \text{area } ACFE$$

$$\therefore \quad W_1 \neq W_2 \neq W_3$$

Thus, the work done depends on the path of the process when the system goes from one therm dynamic state to another.

4.6 Internal Energy (U)

The energy content of a system is called its internal energy. It is the sum of following forms o energy of the system:

(*i*) kinetic energy due to translational, rotational and vibrational motion of the molecules, all o which depend only on the temperature,

(*ii*) potential energy due to intermolecular forces, which depends on the separation between th molecules, and

(*iii*) the energy of electrons and nuclei.

In practice, it is not possible to measure the total internal energy of a system in any given sta Only change in its value can be measured.

If the state of the system is changed from an initial state 1 to a final state 2, by supplying hea to the system and if W is the work done by the system during the change, then increase in the intern energy of the system is given by

$$(U_2 - U_1) = Q - W \qquad \text{...(4.1}$$

where U_1 is the internal energy in state 1, and U_2 the internal energy in state 2.

Internal Energy of a Real gas and Ideal gas

The internal energy of a perfect (or ideal) gas is only dependent upon temperature where as th of a real gas, it is a function of both temperature and volume.

For a perfect gas, the internal energy is only kinetic energy of its molecules. It is proportional kT and hence only depends upon temperature (T), k being Boltzmann's constant. The internal ener of a perfect gas is independent of its volume.

For a real gas, say a gas obeying Van der Waals' equation, the internal energy is the sum of th kinetic and potential energies of molecules due to their mutual forces of attraction. The force attraction between the molecules depends upon the intermolecular distance and is thus a function volume. Hence, for a real gas, internal energy is a function of both, the temperature and volume.

Equation (4.1) is the mathematical statement of the first law of thermodynamics. In a convenie form the law is stated below.

4.7 First Law of Thermodynamics

Statement: When a certain amount of heat Q is supplied to a system which does external wo W in passing from state 1 to state 2, the amount of heat is equal to sum of the increase in the inter energy of the system and the external work done by the system. In symbols, the law is expressed

$$Q = (U_2 - U_1) + W \qquad \text{...(4.}$$

The work done by the composite system $= W + W'$

It means that the heat transferred by the composite system $= Q + Q'$. But the composite system is surrounded by adiabatic walls and the net heat transferred is zero

$$\therefore \quad Q + Q' = 0$$

or

$$Q = -Q' \qquad \text{...(iv)}$$

Thus, for two systems *A* and *B* in thermal contact with each other, and the composite system surrounded by adiabatic walls, the heat gained by one system is equal to the heat lost by the other system.

4.4 Thermodynamic Equilibrium

Any state of homogeneous system in which any two of the three variables *P*, *V* and *T* remain constant, as long as the external conditions remain unchanged is said to be in thermodynamic equilibrium.

A system in thermodynamic equilibrium must satisfy the following requirements strictly :

(*i*) **Mechanical Equilibrium.** For a system to be in mechanical equilibrium, there should be no macroscopic movement within the system (*i.e.* no unbalanced forces acting) or of the system with respect to its surroundings.

(*ii*) **Thermal Equilibrium.** For a system to be in thermal equilibrium, there should be no temperature difference between the parts of the system or between the system and the surroundings.

(*iii*) **Chemical Equilibrium.** For a system to be in chemical equilibrium, there should be no chemical reaction within the system and also no movement of any chemical constituent from one part of the system to the other.

Quasistatic Process

A finite unbalanced force may cause the system to pass through *non-equilibrium* states. A quasistatic process is defined as the process in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through which the system passes during a quasistatic process can be considered as equilibrium states.

A quasistatic process is an ideal concept which can never be satisfied rigorously in practice. However, in actual practice, many processes closely approach a quasistatic process with no significant error.

4.5 Work: A path dependent function

A system can be taken from state *A* to state *B* by many ways as shown in fig. 4.2. Let the coordinates of state *A* and *B* be *A* (P_1, V_1) and *B* (P_2, V_2) respectively, where P_1 and V_1 represents pressure and volume of state *A* and P_2 and V_2 that of state *B*.

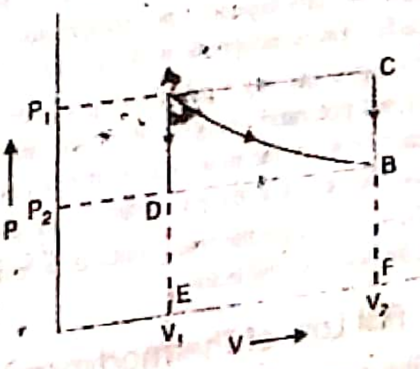


Fig. 4.2

1. Starting from point *A*, the pressure is continuously decreased from P_1 to P_2 along the curve *AB* so that volume increases from V_1 to V_2. The work done by the system is given by

$$W_1 = \int_{V_1}^{V_2} PdV = \text{area } ABFE$$

or

$$F_2(P_B, V_B, P_C, V_C) = 0$$

Also

$$P_B = f_2(V_B, P_C, V_C) \quad \text{...(iii)}$$

From equations (ii) and (iii) for A and C to be in thermal equilibrium separately,

$$f_1(P_A, V_A, V_B) = f_2(V_B, P_C, V_C) \quad \text{...(iv}$$

If A and C are in thermal equilibrium with B separately, then according to the zeroth law, A an

C are also in thermal equilibrium with one another

$$\therefore \quad F_1(P_A, V_A, P_C, V_C) = 0 \quad \text{...(}$$

Equation (iv) contains a variable V_B, whereas equation (v) does not contain the variable V_B

means

$$\phi_1(P_A, V_A) = \phi_3(P_C, V_C) \quad \text{...(}$$

In general,

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B) = \phi_3(P_C, V_C) \quad \text{...(v}$$

These three functions have the same numerical value though the parameters (P, V) of each

different. This numerical value is termed as *temperature* (T) of the body.

$$\phi(P, V) = T \quad \text{...(vi}$$

This is called *the equation of state of the fluid.*

Therefore, the temperature of a system can be defined as the property that determines whether not the body is in thermal equilibrium with the neighbouring systems. If a number of systems are thermal equilibrium, this common property of the system can be represented by a single numeri value called the temperature. It means that if two systems are not in thermal equilibrium, they are different temperatures.

Example. In a mercury glass thermometer, the pressure above the mercury column is zero a volume of mercury measures the temperature. If a thermometer shows a constant reading in t systems A and B seperately, it will show the same reading even when A and B are brought in conta

4.3 Concept of Heat

Heat is defined as *energy in transit*. As it is not possible to speak of work in a body, it is also possible to speak of heat in a body. Work is either done on a body or by a body. Similarly, heat flow from a body or to a body. If a body is at a constant temperature, it has both mechanical thermal energies due to the molecular agitations and it is not possible to separate them. So, in case, we cannot talk of heat energy. It means, if the flow of heat stops, the word heat cannot be us It is only used when there is transfer of energy between two or more systems.

Consider two systems A and B in thermal contact with one another and surrounded by adia walls.

For the system A,

$$Q' = U_2 - U_1 + W$$

where Q is the heat energy transferred, U_1 is the initial internal energy, U_2 is the final internal en and W is the work done.

Similarly for the system B

$$Q' = U' - U_1' + W'$$

Adding (i) and (ii)

$$\therefore \quad Q + Q' = (U_2 - U_1) + W + (U_2' - U_1') + W'$$

$$Q + Q' = [(U_2 + U_2') - (U_1 + U_1')] + (W + W')$$

The total change in the internal energy of the composite system

$$= [(U_2 + U_2') - (U_1 + U_1')]$$

(iii) Isolated system: A system which is thermall insulated and has no communication of heat or work with the surroundings is called *isolated system*.

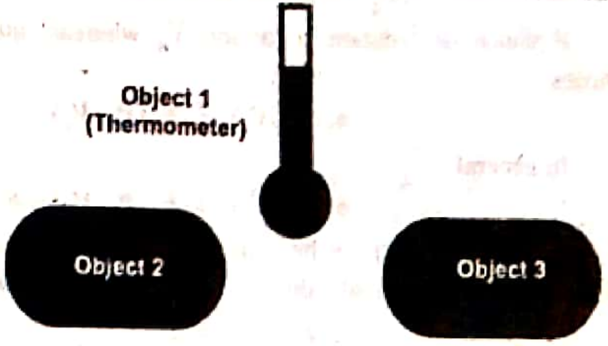
4.2 Zeroth Law of Thermodynamics

When a hot body A is brought in thermal contact with a cold body *B*, heat flows from *A* to *B* and after some time the flow stops. The bodies are then said to be in thermal equilibrium with each other.

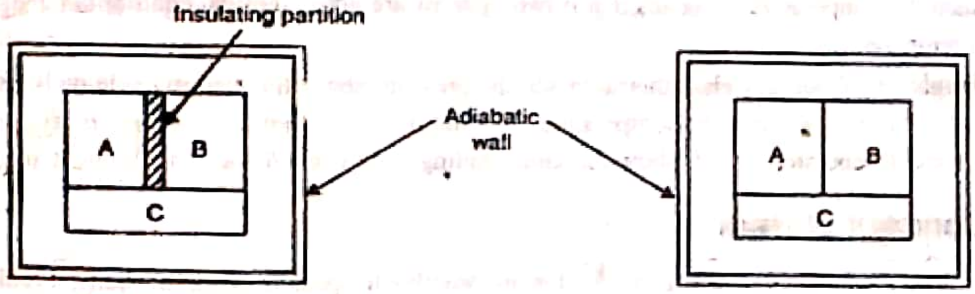
Statement: *The zeroth law of thermodynamics states that if two bodies A and B are each separately in thermal equilibrium with a third body C, then A and B are also in thermal equilibrium with each other.*

Explanation: We consider two systems *A* and *B* insulated from each other but in good thermal contact with a common system *C*. Systems *A* and *B* will attain thermal equilibrium with third system *C* [Fig. 4.1 (*a*)].

Thermodynamic Equilibrium (Zeroth Law)



When two objects are separately in the thermodynamic equilibrium with a third object *d*, then both are in thermodynamic equilibrium with each other.



(*a*) (*b*)

Fig. 4.1

Now if the insulating partition is removed and systems *A* and *B* are brought into thermal contact, we find that there is no further change. This means that the systems *A* and *B* are also in thermal equilibrium with another. This is known as zeroth law of thermodynamics.

Conversely the law can be stated as follows:

If three or more systems are in thermal contact, each to each, by means of diathermal walls and are all in thermal equilibrium together, then any two systems taken separately are in thermal equilibrium with one another.

Consider three fluids *A*, *B* and *C*. Let P_A, V_A represent the pressure and volume of *A*, P_B, V_B, the pressure and volume of *B*, and P_C, V_C are the pressure and volume of *C*.

If *A* and *B* are in thermal equilibrium, then

$$\phi_1 (P_A, V_A) = \phi_2 (P_B, V_B)$$

or

$$F_1 (P_A, V_A, P_B, V_B) = 0 \quad (i)$$

Expression (*i*) can be solved, and

$$P_B = f_1 (P_A, V_A, V_B) \quad (ii)$$

If *B* and *C* are in thermal equilibrium

$$\phi_2 (P_B, V_B) = \phi_3 (P_C, V_C)$$

A system may be separated from its surroundings by a real or imaginary boundary through which heat or mechanical energy may pass. The existence of the boundary is, however, essential to visualize the system distinctly from rest of the universe. A thermodynamic system may contain no substance at all, but may consist of radiant energy or electric and magnetic field. The combination of a system and its surroundings is called an *universe*.

Thermodynamic Variables and equation of state

The thermodynamic state or macroscopic state of a system is determined by four observable properties. These properties are the composition, pressure, volume and temperature, and are called the *variables of state*. For a homogeneous system, consisting of a single substance, the composition is fixed. Hence the state of the system is determined completely by the three variables: pressure (P), volume (V) and temperature (T).

For a system, in general, there is an equation of state

$$f(P, V, T) = 0$$

Therefore, the pressure, volume and temperature are not independent variables. Consequently the thermodynamic state of a homogeneus system is determined completely by knowing two out of three variables.

For example: the equation of state for an ideal gas in a static condition is represented as

$$PV = RT$$

where R is universal gas constant.

For a Van der Waals' gas, the equation of state is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where a and b are Van der Waal's constants.

Limitations

(*i*) The equation of state is not applicable to systems which are not in thermodynamic equilibrium.

(*ii*) Every thermodynamic system has its own equation of state independent of the others.

(*iii*) An equation of state expresses the peculiar behaviour of one individual system which distinguishes it from the others.

(*iv*) An equation of state is not a theoretical deduction from thermodynamics but is an exper mental backing to it.

The thermodynamic systems in engineering are gas, vapour, steam, mixture of gasoline vapo and air, ammonia vapours and its liquid. In physics, thermodynamics includes besides the abov systems like stretched wires, thermocouples, magnetic materials, electrical condenser, electrical reversible cells, solid and surface films etc.

There are three classes of system

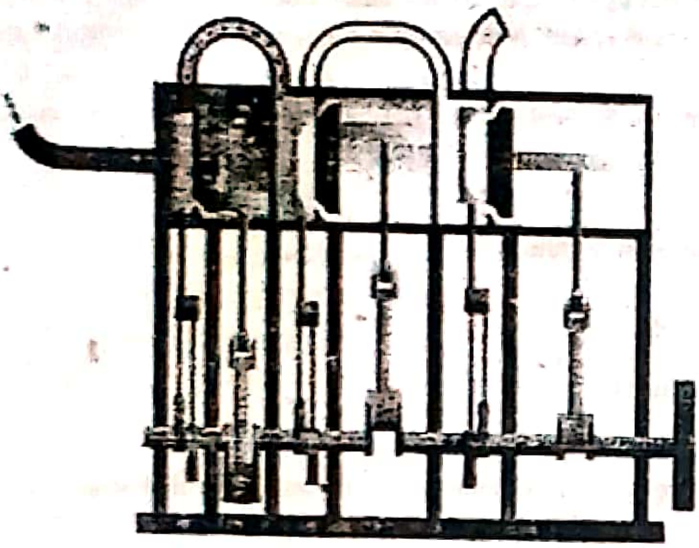
(*i*) **Open system :** A system which can exchange matter and energy with the surroundings called an *open system*. e.g. Air compressor : Air at low pressure enters and air at high pressure leav the system i.e. there is an exchange of matter and energy with the surroundings.

(*ii*) **Closed system :** A system which can exchange only energy (and not matter) with the s roundings is called a *closed system*. e.g., Gas enclosed in a cylinder expands when heated and dr the piston outwards. The boundary of the system moves but the matter (here gas) in the system mains constant.

Laws of Thermodynamics

4

AT A GLANCE



• Thermodynamic System • Zeroth Law of Thermodynamics • Concept of Heat • Thermodynamic Equilibrium • Work A Path Dependent Function • Internal Energy (U) • First Law of Thermodynamics • Internal Energy as a State Function • Specific Heats of a Gas • Applications of First Law of Thermodynamics • The Indicator Diagram • Work done during an Isothermal Process • Work done during an Adiabatic Process • Slopes of Adiabatics and Isothermals • Relation between Adiabatic & Isothermal Elasticities • Cooling due to Adiabatic Reversible Process • Clement and Desormes Method-Determination of γ • Partington's Method • Ruchhardt's Experiment • Reversible and Irreversible Process • Heat Engines • Definition of Efficiency • Carnot's Ideal Heat Engine • Carnot's Cycle • Effective way to Increase Efficiency • Carnot's Engine and Refrigerator • Coefficient of Performance • Second Law of Thermodynamics • Carnot's Theorem • Steam Engine • Otto Cycle • Petrol Engine • Diesel Engine • Multicylinder Engine

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4.1 Thermodynamic System

A system may be defined as a definite quantity of matter (solid, liquid or gases) bounded by some closed surface. The simplest example of a system is a gas contained in a cylinder with a movable piston. When a system is completely uniform throughout, such as gas, or mixture of gases, or a pure solid, or a liquid or a solution is called a homogeneous system. When a system consists of two or more phases which are separated from one another by definite boundary surfaces, it is said to be a heterogeneous system. Examples of heterogeneous system are: a liquid and its vapour, two immiscible or partially miscible liquids. Anything outside this system which can exchange energy with it and has a direct bearing on the behaviour of the system is called as its **surroundings**.