



# Chapter 14 Thermodynamics



Thermodynamics is a branch of science which deals with exchange of heat energy between bodies and conversion of the heat energy into mechanical energy and vice-versa.

## Some Definitions

### (i) Thermodynamic system

(i) It is a collection of an extremely large number of atoms or molecules

(ii) It is confined with in certain boundaries.

(iii) Anything outside the thermodynamic system to which energy or matter is exchanged is called its surroundings.

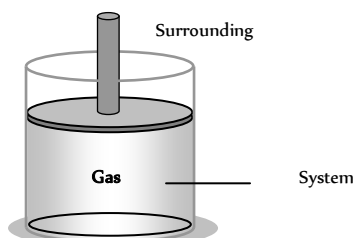


Fig. 14.1

(iv) Thermodynamic system may be of three types

(a) Open system : It exchange both energy and matter with the surrounding.

(b) Closed system : It exchange only energy (not matter) with the surroundings.

(c) Isolated system : It exchange neither energy nor matter with the surrounding.

(2) **Thermodynamic variables and equation of state** : A thermodynamic system can be described by specifying its pressure, volume, temperature, internal energy and the number of moles. These parameters are called thermodynamic variables. The relation between the thermodynamic variables ( $P$ ,  $V$ ,  $T$ ) of the system is called equation of state.

For  $\mu$  moles of an ideal gas, equation of state is  $PV = \mu RT$  and for 1 mole of an it ideal gas is  $PV = RT$

(3) **Thermodynamic equilibrium** : In steady state thermodynamic variables are independent of time and the system is said to be in the state of thermodynamic equilibrium. For a system to be in thermodynamic equilibrium, the following conditions must be fulfilled.

(i) Mechanical equilibrium : There is no unbalanced force between the system and its surroundings.

(ii) Thermal equilibrium : There is a uniform temperature in all parts of the system and is same as that of surrounding.

(iii) Chemical equilibrium : There is a uniform chemical composition through out the system and the surrounding.

(4) **Thermodynamic process** : The process of change of state of a system involves change of thermodynamic variables such as pressure  $P$ , volume  $V$  and temperature  $T$  of the system. The process is known as thermodynamic process. Some important processes are

(i) Isothermal process : Temperature remain constant

(ii) Adiabatic process : No transfer of heat

(iii) Isobaric process : Pressure remains constant

(iv) Isochoric (isovolumic process) : Volume remains constant

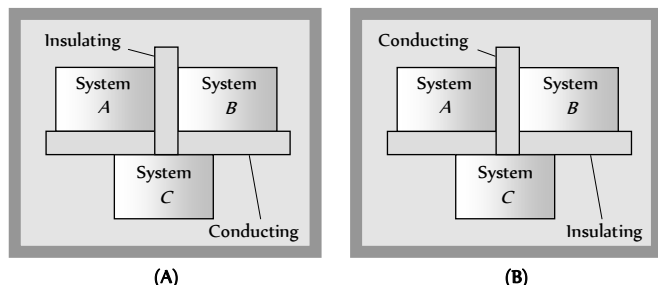
(v) Cyclic and non-cyclic process : Incyclic process Initial and final states are same while in non-cyclic process these states are different.

(vi) Reversible and irreversible process :

(5) **Indicator diagram** : Whenever the state of a gas ( $P, V, T$ ) is changed, we say the gaseous system is undergone a thermodynamic process. The graphical representation of the change in state of a gas by a thermodynamic process is called indicator diagram. Indicator diagram is plotted generally in pressure and volume of gas.

## Zeroth Law of Thermodynamics

If systems  $A$  and  $B$  are each in thermal equilibrium with a third system  $C$ , then  $A$  and  $B$  are in thermal equilibrium with each other.



(1) The zeroth law leads to the concept of temperature. All bodies in thermal equilibrium must have a common property which has the same value for all of them. This property is called the temperature.

(2) The zeroth law came to light long after the first and second laws of thermodynamics had been discovered and numbered. It is so named because it logically precedes the first and second laws of thermodynamics.

## Heat, Internal Energy and Work in Thermodynamics

(1) **Heat ( $\Delta Q$ )** : It is the energy that is transferred between a system and its environment because of the temperature difference between them.

(i) Heat is a path dependent quantity *e.g.* Heat required to change the temperature of a given gas at a constant pressure is different from that required to change the temperature of same gas through same amount at constant volume.

(ii) For gases when heat is absorbed and temperature changes  $\Rightarrow \Delta Q = \mu C \Delta T$

At constant pressure  $(\Delta Q)_p = \mu C_p \Delta T$

At constant volume  $(\Delta Q)_v = \mu C_v \Delta T$

(2) **Internal energy ( $U$ )** : Internal energy of a system is the energy possessed by the system due to molecular motion and molecular configuration.

The energy due to molecular motion is called internal kinetic energy  $U_K$  and that due to molecular configuration is called internal potential energy  $U_p$ , *i.e.* Total internal energy  $U = U_K + U_p$

(i) For an ideal gas, as there is no molecular attraction  $U_p = 0$

*i.e.* internal energy of an ideal gas is totally kinetic and is given by

$$U = U_K = \frac{3}{2} \mu R T \text{ and change in internal energy } \Delta U = \frac{3}{2} \mu R \Delta T$$

(ii) In case of gases whatever be the process

$$\Delta U = \mu \frac{f}{2} R \Delta T = \mu C_v \Delta T = \mu \frac{R}{(\gamma - 1)} \Delta T = \frac{\mu R (T_f - T_i)}{\gamma - 1}$$

$$= \frac{\mu R T_f - \mu R T_i}{\gamma - 1} = \frac{(P_f V_f - P_i V_i)}{\gamma - 1}$$

(iii) Change in internal energy does not depend on the path of the process. So it is called a point function *i.e.* it depends only on the initial and final states of the system, *i.e.*  $\Delta U = U_f - U_i$

(3) **Work ( $\Delta W$ )** : Suppose a gas is confined in a cylinder that has a movable piston at one end. If  $P$  be the pressure of the gas in the cylinder, then force exerted by the gas on the piston of the cylinder  $F = PA$  ( $A$  = Area of cross-section of piston)

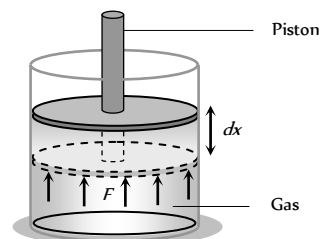


Fig. 14.4

When the piston is pushed outward an infinitesimal distance  $dx$ , the work done by the gas  $dW = F \cdot dx = P(A \cdot dx) = P dV$

For a finite change in volume from  $V_i$  to  $V_f$

$$\text{Total amount of work done } W = \int_{V_i}^{V_f} P dV = P(V_f - V_i)$$

(i) If we draw indicator diagram, the area bounded by  $PV$ -graph and volume axis represents the work done

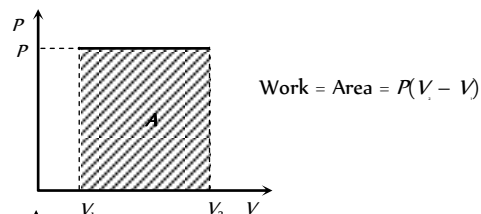


Fig. 14.5

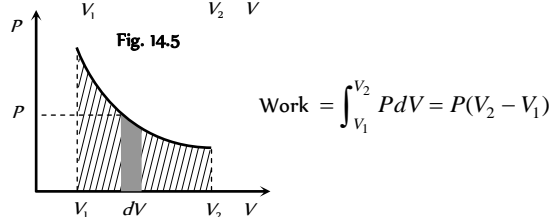


Fig. 14.6

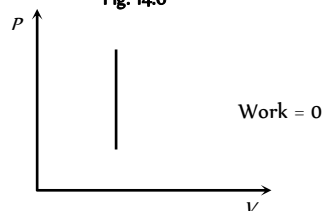


Fig. 14.7

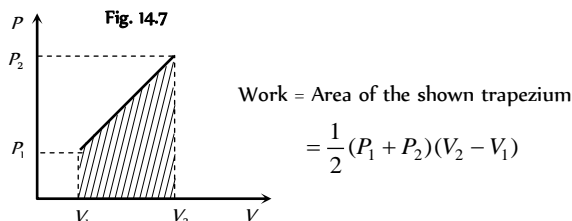


Fig. 14.8

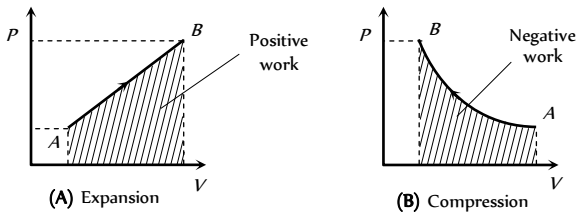
(ii) From  $\Delta W = P \Delta V = P(V_f - V_i)$

If system expands against some external force then  $V_f > V_i$

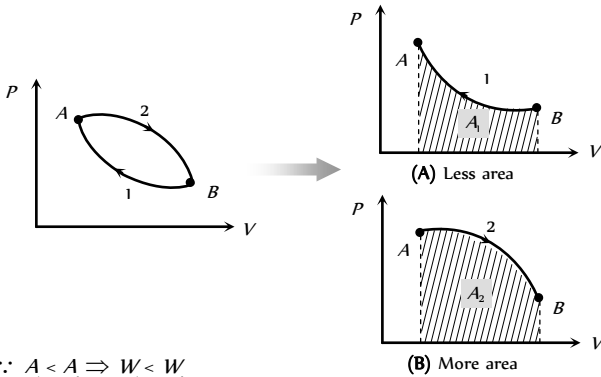
$\Rightarrow \Delta W = \text{positive}$

If system contracts because of external force then  $V_f < V_i$

$\Rightarrow \Delta W = \text{negative}$

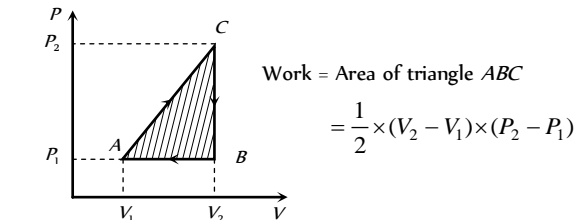


(iii) Like heat, work done is also depends upon initial and final state of the system and path adopted for the process

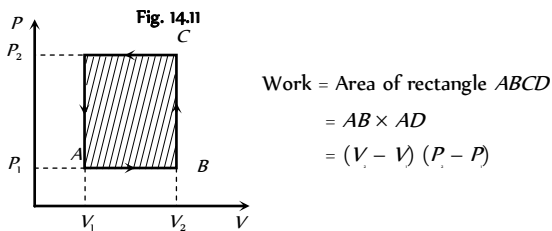


$\therefore A_1 < A_2 \Rightarrow W_1 < W_2$

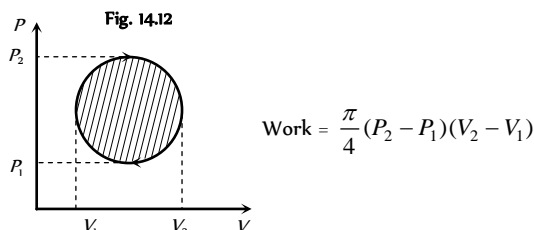
(iv) In cyclic process, work done is equal to the area of closed curve. It is positive if the cycle is clockwise and it is negative if the cycle is anticlockwise.



$$\begin{aligned} \text{Work} &= \text{Area of triangle } ABC \\ &= \frac{1}{2} \times (V_2 - V_1) \times (P_2 - P_1) \end{aligned}$$



$$\begin{aligned} \text{Work} &= \text{Area of rectangle } ABCD \\ &= AB \times AD \\ &= (V_2 - V_1) (P_2 - P_1) \end{aligned}$$



$$\text{Work} = \frac{\pi}{4} (P_2 - P_1) (V_2 - V_1)$$

## First Law of Thermodynamics (FLOT)

(1) It is a statement of conservation of energy in thermodynamical process.

(2) According to it heat given to a system ( $\Delta Q$ ) is equal to the sum of increase in its internal energy ( $\Delta U$ ) and the work done ( $\Delta W$ ) by the system against the surroundings.

$$\Delta Q = \Delta U + \Delta W$$

(3) It makes no distinction between work and heat as according to it the internal energy (and hence temperature) of a system may be increased either by adding heat to it or doing work on it or both.

(4)  $\Delta Q$  and  $\Delta W$  are the path functions but  $\Delta U$  is the point function.

(5) In the above equation all three quantities  $\Delta Q$ ,  $\Delta U$  and  $\Delta W$  must be expressed either in *Joule* or in *calorie*.

(6) The first law introduces the concept of internal energy.

(7) Limitation : First law of thermodynamics does not indicate the direction of heat transfer. It does not tell anything about the conditions, under which heat can be transformed into work and also it does not indicate as to why the whole of heat energy cannot be converted into mechanical work continuously.

Table 14.1 : Useful sign convention in thermodynamics

Quantity	Sign	Condition
$\Delta Q$	+	When heat is supplied to a system
	-	When heat is drawn from the system
$\Delta W$	+	When work done by the gas (expansion)
	-	When work done on the gas (compression)
$\Delta U$	+	With temperature rise, internal energy increases
	-	With temperature fall, internal energy decreases

## Isobaric Process

When a thermodynamic system undergoes a physical change in such a way that its pressure remains constant, then the change is known as isobaric process.

(1) **Equation of state** : In this process  $V$  and  $T$  changes but  $P$  remains constant. Hence Charles's law is obeyed in this process.

$$\text{Hence if pressure remains constant } V \propto T \Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

(2) **Indicator diagram** : Graph 1 represent isobaric expansion, graph 2 represent isobaric compression.

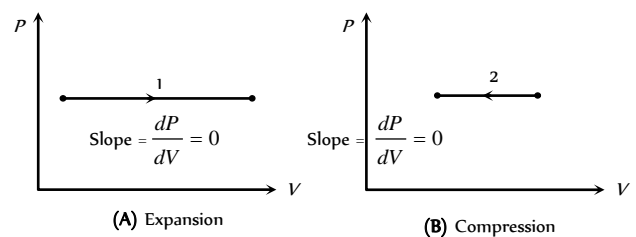


Fig. 14.14

(i) In isobaric expansion (Heating)

Temperature  $\longrightarrow$  increases so  $\Delta U$  is positive

Volume  $\longrightarrow$  increases so  $\Delta W$  is positive

Heat  $\longrightarrow$  flows into the system so  $\Delta Q$  is positive

(ii) In isobaric compression (Cooling)

Temperature  $\longrightarrow$  decreases so  $\Delta U$  is negative

Volume  $\longrightarrow$  decreases so  $\Delta W$  is negative

Heat  $\longrightarrow$  flows out from the system so  $\Delta Q$  is negative

(3) **Specific heat** : Specific heat of gas during isobaric process

$$C_p = \left(\frac{f}{2} + 1\right)R$$

(4) **Bulk modulus of elasticity** :  $K = \frac{\Delta P}{-\frac{\Delta V}{V}} = 0$  [As  $\Delta P = 0$ ]

(5) **Work done in isobaric process**

$$\Delta W = \int_{V_i}^{V_f} P dV = P \int_{V_i}^{V_f} dV = P[V_f - V_i] \quad [\text{As } P = \text{constant}]$$

$$\Rightarrow \Delta W = P(V_f - V_i) = \mu R[T_f - T_i] = \mu R \Delta T$$

(6) **FLOT in isobaric process** : From  $\Delta Q = \Delta U + \Delta W$

$$\therefore \Delta U = \mu C_v \Delta T = \mu \frac{R}{(\gamma - 1)} \Delta T \quad \text{and} \quad \Delta W = \mu R \Delta T$$

$$\Rightarrow (\Delta Q)_p = \mu \frac{R}{(\gamma - 1)} \Delta T + \mu R \Delta T = \mu \left(\frac{\gamma}{\gamma - 1}\right) R \Delta T = \mu C_p \Delta T$$

(7) **Examples of isobaric process** : All state changes occurs at constant temperature and pressure.

Boiling of water

(i) Water  $\longrightarrow$  vapours

(ii) Temperature  $\longrightarrow$  constant

(iii) Volume  $\longrightarrow$  increases

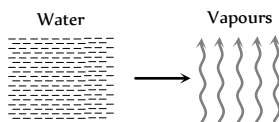


Fig. 14.15

(iv) A part of heat supplied is used to change volume (expansion) against external pressure and remaining part is used to increase its potential energy (kinetic energy remains constant)

$$(v) \text{ From FLOT } \Delta Q = \Delta U + \Delta W \Rightarrow mL = \Delta U + P(V_f - V_i)$$

Freezing of water

(i) Water  $\longrightarrow$  ice

(ii) Temperature  $\longrightarrow$  constant

(iii) Volume  $\longrightarrow$  increases

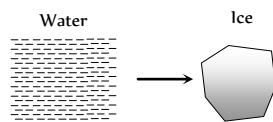


Fig. 14.16

(iv) Heat is given by water itself. It is used to do work against external atmospheric pressure and to decrease the internal potential energy.

$$(v) \text{ From FLOT } \Delta Q = \Delta U + \Delta W \Rightarrow -mL = \Delta U + P(V_f - V_i)$$

## Isochoric or Isometric Process

When a thermodynamic process undergoes a physical change in such a way that its volume remains constant, then the change is known as isochoric process.

(i) **Equation of state** : In this process  $P$  and  $T$  changes but  $V =$  constant. Hence Gay-Lussac's law is obeyed in this process i.e.  $P \propto T \Rightarrow$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \text{constant}$$

(2) **Indicator diagram** : Graph 1 and 2 represent isometric increase in pressure at volume  $V_1$  and isometric decrease in pressure at volume  $V_2$

respectively and slope of indicator diagram  $\frac{dP}{dV} = \infty$

(i) Isometric heating

(a) Pressure  $\longrightarrow$  increases

(b) Temperature  $\longrightarrow$  increases

(c)  $\Delta Q \longrightarrow$  positive

(d)  $\Delta U \longrightarrow$  positive

(ii) Isometric cooling

(a) Pressure  $\longrightarrow$  decreases

(b) Temperature  $\longrightarrow$  decreases

(c)  $\Delta Q \longrightarrow$  negative

(d)  $\Delta U \longrightarrow$  negative

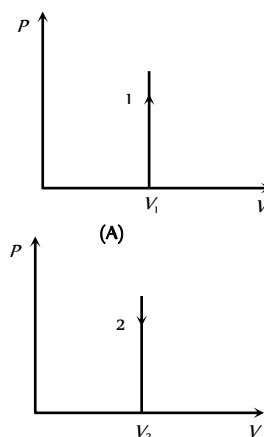


Fig. 14.17

(3) **Specific heat** : Specific heat of gas during isochoric process

$$C_v = \frac{f}{2}R$$

(4) **Bulk modulus of elasticity** :  $K = \frac{\Delta P}{-\frac{\Delta V}{V}} = \frac{\Delta P}{0} = \infty$

(5) **Work done in isochoric process**

$$\Delta W = P\Delta V = P[V_f - V_i] = 0 \quad [\text{As } V = \text{constant}]$$

(6) **FLOT in isochoric process** : From  $\Delta Q = \Delta U + \Delta W$

$$\therefore \Delta W = 0 \Rightarrow (\Delta Q)_v = \Delta U = \mu C_v \Delta T = \mu \frac{R}{\gamma - 1} \Delta T = \frac{P_f V_f - P_i V_i}{\gamma - 1}$$

## Isothermal Process

When a thermodynamic system undergoes a physical change in such a way that its temperature remains constant, then the change is known as isothermal changes.

(i) **Essential condition for isothermal process**

(i) The walls of the container must be perfectly conducting to allow free exchange of heat between the gas and its surrounding.

(ii) The process of compression or expansion should be so slow so as to provide time for the exchange of heat.

Since these two conditions are not fully realised in practice, therefore, no process is perfectly isothermal.

(2) **Equation of state** : In this process,  $P$  and  $V$  change but  $T =$  constant i.e. change in temperature  $\Delta T = 0$ .

Boyle's law is obeyed i.e.  $PV = \text{constant} \Rightarrow P_f V_f = P_i V_i$

(3) **Example of isothermal process** : Melting of ice (at  $0^\circ\text{C}$ ) and boiling of water (at  $100^\circ\text{C}$ ) are common example of this process.

(4) **Indicator diagram** : According to  $PV = \text{constant}$ , graph between  $P$  and  $V$  is a part of rectangular hyperbola. The graphs at different temperature are parallel to each other are called isotherms.

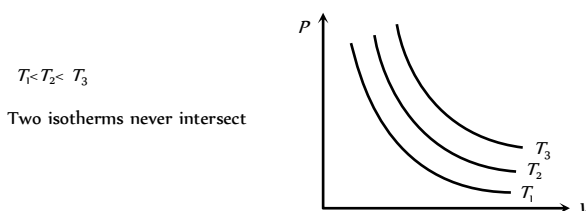


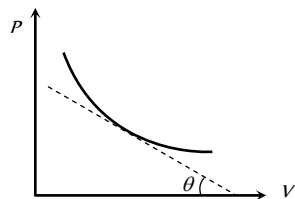
Fig. 14.18

(i) Slope of isothermal curve : By differentiating  $PV = \text{constant}$ . We get

$$P dV + V dP = 0$$

$$\Rightarrow P dV = -V dP$$

$$\Rightarrow \text{Slope} = \tan \theta = \frac{dP}{dV} = -\frac{P}{V}$$



(ii) Area between the isotherm and volume axis represents the work done in isothermal process.

If volume increases  $\Delta W = +$  (Area under curve) and if volume decreases  $\Delta W = -$  (Area under curve)

(5) **Specific heat** : Specific heat of gas during isothermal change is infinite. As  $C = \frac{Q}{m \Delta T} = \frac{Q}{m \times 0} = \infty$  [As  $\Delta T = 0$ ]

(6) **Isothermal elasticity ( $E_\theta$ )** : For this process  $PV = \text{constant}$ .

$$\Rightarrow P dV = -V dP \Rightarrow P = \frac{dP}{-dV/V} = \frac{\text{Stress}}{\text{Strain}} = E_\theta$$

$$\Rightarrow E_\theta = P \text{ i.e. isothermal elasticity is equal to pressure}$$

At N.T.P.,  $E_\theta = \text{Atmospheric pressure} = 1.01 \times 10^5 \text{ N/m}^2$

(7) **Work done in isothermal process**

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{\mu RT}{V} dV \quad [\text{As } PV = \mu RT]$$

$$W = \mu RT \log_e \left( \frac{V_f}{V_i} \right) = 2.303 \mu RT \log_{10} \left( \frac{V_f}{V_i} \right)$$

$$\text{or } W = \mu RT \log_e \left( \frac{P_i}{P_f} \right) = 2.303 \mu RT \log_{10} \left( \frac{P_i}{P_f} \right)$$

(8) **FLOT in isothermal process** : From  $\Delta Q = \Delta U + \Delta W$

$$\therefore \Delta U = 0 \quad [\text{As } \Delta T = 0] \Rightarrow \Delta Q = \Delta W$$

i.e. heat supplied in an isothermal change is used to do work against external surrounding.

or if the work is done on the system than equal amount of heat energy will be liberated by the system.

## Adiabatic Process

When a thermodynamic system undergoes a change in such a way that no exchange of heat takes place between System and surroundings, the process is known as adiabatic process.

In this process  $P$ ,  $V$  and  $T$  changes but  $\Delta Q = 0$ .

(1) **Essential conditions for adiabatic process**

(i) There should not be any exchange of heat between the system and its surroundings. All walls of the container and the piston must be perfectly insulating.

(ii) The system should be compressed or allowed to expand suddenly so that there is no time for the exchange of heat between the system and its surroundings.

Since, these two conditions are not fully realised in practice, so no process is perfectly adiabatic.

(2) **Some examples of adiabatic process**

(i) Sudden compression or expansion of a gas in a container with perfectly non-conducting walls.

(ii) Sudden bursting of the tube of bicycle tyre.

(iii) Propagation of sound waves in air and other gases.

(iv) Expansion of steam in the cylinder of steam engine.

(3) **FLOT in adiabatic process** : From  $\Delta Q = \Delta U + \Delta W$

$$\text{For adiabatic process } \Delta Q = 0 \Rightarrow \Delta U = -\Delta W$$

If  $\Delta W = \text{positive}$  then  $\Delta U = \text{negative}$  so temperature decreases i.e. adiabatic expansion produce cooling.

If  $\Delta W = \text{negative}$  then  $\Delta U = \text{positive}$  so temperature increases i.e. adiabatic compression produce heating.

(4) **Equation of state** : In adiabatic change ideal gases do not obeys Boyle's law but obeys Poisson's law. According to it

$$PV^\gamma = \text{constant; where } \gamma = \frac{C_p}{C_v}$$

(i) For temperature and volume

$$TV^\gamma = \text{constant} \Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \text{ or } T \propto V^{1-\gamma}$$

(ii) For temperature and pressure

$$\frac{T^\gamma}{P^{\gamma-1}} = \text{const.} \Rightarrow T_1^\gamma P_1^{1-\gamma} = T_2^\gamma P_2^{1-\gamma} \text{ or } T \propto P^{\frac{\gamma-1}{\gamma}} \text{ or } P \propto T^{\frac{\gamma}{\gamma-1}}$$

Table 14.2 : Special cases of adiabatic process

Type of gas	$P \propto \frac{1}{V^\gamma}$	$P \propto T^{\frac{\gamma}{\gamma-1}}$	$T \propto \frac{1}{V^{\gamma-1}}$
Monoatomic $\gamma = 5/3$	$P \propto \frac{1}{V^{5/3}}$	$P \propto T^{5/2}$	$T \propto \frac{1}{V^{2/3}}$
Diatomic $\gamma = 7/5$	$P \propto \frac{1}{V^{7/5}}$	$P \propto T^{7/2}$	$T \propto \frac{1}{V^{2/5}}$
Polyatomic $\gamma = 4/3$	$P \propto \frac{1}{V^{4/3}}$	$P \propto T^4$	$T \propto \frac{1}{V^{1/3}}$

(5) **Indicator diagram**

(i) Curve obtained on  $PV$  graph are called adiabatic curve.

(ii) Slope of adiabatic curve : From  $PV^\gamma = \text{constant}$

By differentiating, we get

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

$$\frac{dP}{dV} = -\gamma \frac{P V^{\gamma-1}}{V^\gamma} = -\gamma \left( \frac{P}{V} \right)$$

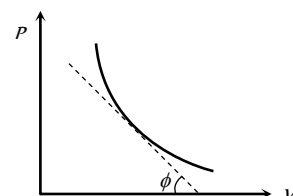


Fig. 14.20

$$\therefore \text{Slope of adiabatic curve } \tan \phi = -\gamma \left( \frac{P}{V} \right)$$

$$(iii) \text{ But we also know that slope of isothermal curve } \tan \theta = \frac{-P}{V}$$

$$\text{Hence } (\text{Slope})_{ad} = \gamma \times (\text{Slope})_{is} \text{ or } \frac{(\text{Slope})_{adi}}{(\text{Slope})_{iso}} > 1$$

(6) **Specific heat** : Specific heat of a gas during adiabatic change is

$$\text{zero As } C = \frac{Q}{m\Delta T} = \frac{0}{m\Delta T} = 0 \quad [\text{As } Q = 0]$$

(7) **Adiabatic elasticity ( $E_\phi$ )** :  $PV^\gamma = \text{constant}$

Differentiating both sides  $d(PV^\gamma) + PV^{\gamma-1}dV = 0$

$$\gamma P = \frac{dP}{-dV/V} = \frac{\text{Stress}}{\text{Strain}} = E_\phi \Rightarrow E_\phi = \gamma P$$

i.e. adiabatic elasticity is  $\gamma$  times that of pressure

$$\text{Also isothermal elasticity } E_\theta = P \Rightarrow \frac{E_\phi}{E_\theta} = \gamma = \frac{C_p}{C_v}$$

i.e. the ratio of two elasticity of gases is equal to the ratio of two specific heats.

(8) **Work done in adiabatic process**

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{K}{V^\gamma} dV \Rightarrow W = \frac{[P_i V_i - P_f V_f]}{(\gamma - 1)} = \frac{\mu R(T_i - T_f)}{(\gamma - 1)}$$

(As  $PV^\gamma = K$ ,  $PV = \mu RT$ , and  $PV = \mu RT$ )

(i)  $W \propto$  quantity of gas (either  $M$  or  $\mu$ )

(ii)  $W \propto$  temperature difference ( $T_i - T_f$ )

$$(iii) W \propto \frac{1}{\gamma - 1} \quad \because \gamma_{mono} > \gamma_{di} > \gamma_{tri} \Rightarrow W_{-} < W_{-} < W_{-}$$

(9) **Comparison between isothermal and adiabatic indicator diagrams :**

Always remember that adiabatic curves are more steeper than isothermal curves

(i) Equal expansion : Graph 1 represent isothermal process and 2 represent adiabatic process

$$W_{isotherm} > W_{adiabatic}$$

$$P_{isotherm} > P_{adiabatic}$$

$$T_{isotherm} > T_{adiabatic}$$

$$(\text{Slope})_{isotherm} < (\text{Slope})_{adiabatic}$$

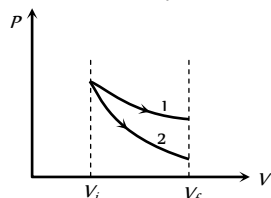


Fig. 14.21

(ii) Compression : Graph 1 represent adiabatic process and 2 represent isothermal process

$$W_{adiabatic} > W_{isotherm}$$

$$P_{adiabatic} > P_{isotherm}$$

$$T_{adiabatic} > T_{isotherm}$$

$$(\text{Slope})_{adiabatic} < (\text{Slope})_{isotherm}$$

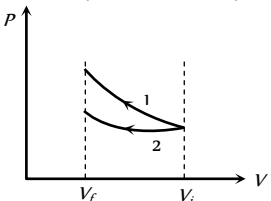


Fig. 14.22

(10) **Free expansion** : Free expansion is adiabatic process in which no work is performed on or by the system. Consider two vessels placed in a system which is enclosed with thermal insulation (asbestos-covered). One vessel contains a gas and the other is evacuated. When suddenly the stopcock is opened, the gas rushes into the evacuated vessel and expands freely.

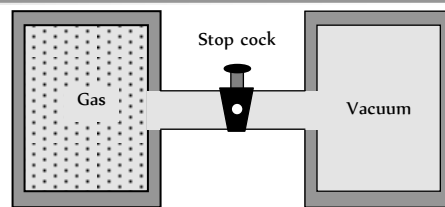


Fig. 14.23

$\Delta W = 0$  (Because walls are rigid)

$\Delta Q = 0$  (Because walls are insulated)

$\Delta U = U_f - U_i = 0$  (Because  $\Delta Q$  and  $\Delta W$  are zero. Thus the final and initial energies are equal in free expansion.)

## Cyclic and Non-cyclic Process

A cyclic process consists of a series of changes which return the system back to its initial state.

In non-cyclic process the series of changes involved do not return the system back to its initial state.

$$(1) \text{ In case of cyclic process as } U_f = U_i \Rightarrow \Delta U = U_f - U_i = 0$$

i.e. change in internal energy for cyclic process is zero and also  $\Delta U \propto \Delta T \Rightarrow \Delta T = 0$  i.e. temperature of system remains constant.

$$(2) \text{ From FLOT } \Delta Q = \Delta U + \Delta W \Rightarrow \Delta Q = \Delta W$$

i.e. heat supplied is equal to the work done by the system.

(3) For cyclic process  $P$ - $V$  graph is a closed curve and area enclosed by the closed path represents the work done.

If the cycle is clockwise work done is positive and if the cycle is anticlockwise work done is negative.

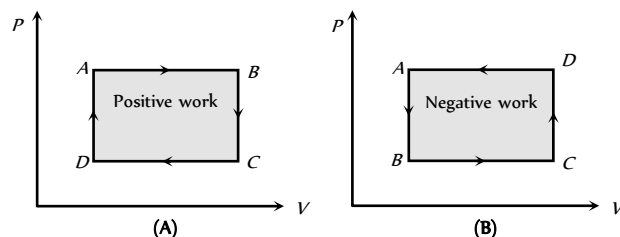


Fig. 14.24

(4) Work done in non cyclic process depends upon the path chosen or the series of changes involved and can be calculated by the area covered between the curve and volume axis on  $PV$  diagram.

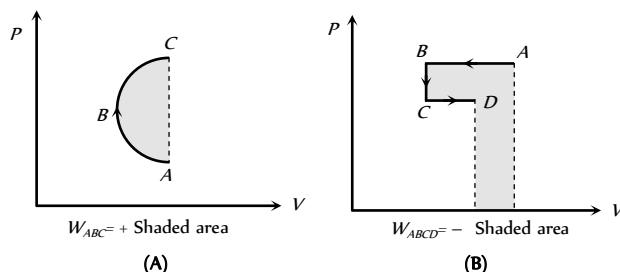


Fig. 14.25

## Quasi Static Process

When we perform a process on a given system, its state is, in general, changed. Suppose the initial state of the system is described by the values  $P_1, V_1, T_1$  and the final state by  $P_2, V_2, T_2$ . If the process is performed in such a way that at any instant during the process, the system is very nearly in thermodynamic equilibrium, the process is called quasi-static. This means, we can specify the parameters  $P, V, T$  uniquely at any instant during such a process.

Actual processes are not quasi-static. To change the pressure of a gas, we can move a piston inside the enclosure. The gas near the piston is acted upon by piston. The pressure of the gas may not be uniform everywhere while the piston is moving. However, we can move the piston very slowly to make the process as close to quasi-static as we wish. Thus, a quasi-static process is an idealised process in which all changes take place infinitely slowly.

## Reversible and Irreversible Process

(1) **Reversible process** : A reversible process is one which can be reversed in such a way that all changes occurring in the direct process are exactly repeated in the opposite order and inverse sense and no change is left in any of the bodies taking part in the process or in the surroundings. For example if heat is absorbed in the direct process, the same amount of heat should be given out in the reverse process, if work is done on the working substance in the direct process then the same amount of work should be done by the working substance in the reverse process. The conditions for reversibility are

(i) There must be complete absence of dissipative forces such as friction, viscosity, electric resistance etc.

(ii) The direct and reverse processes must take place infinitely slowly.

(iii) The temperature of the system must not differ appreciably from its surroundings.

Some examples of reversible process are

(a) All isothermal and adiabatic changes are reversible if they are performed very slowly.

(b) When a certain amount of heat is absorbed by ice, it melts. If the same amount of heat is removed from it, the water formed in the direct process will be converted into ice.

(c) An extremely slow extension or contraction of a spring without setting up oscillations.

(d) When a perfectly elastic ball falls from some height on a perfectly elastic horizontal plane, the ball rises to the initial height.

(e) If the resistance of a thermocouple is negligible there will be no heat produced due to Joule's heating effect. In such a case heating or cooling is reversible. At a junction where a cooling effect is produced due to Peltier effect when current flows in one direction and equal heating effect is produced when the current is reversed.

(f) Very slow evaporation or condensation.

It should be remembered that the conditions mentioned for a reversible process can never be realised in practice. Hence, a reversible process is only an ideal concept. In actual process, there is always loss of heat due to friction, conduction, radiation etc.

(2) **Irreversible process** : Any process which is not reversible exactly is an irreversible process. All natural processes such as conduction, radiation, radioactive decay etc. are irreversible. All practical processes such as free expansion, Joule-Thomson expansion, electrical heating of a wire are also irreversible. Some examples of irreversible processes are given below

(i) When a steel ball is allowed to fall on an inelastic lead sheet, its kinetic energy changes into heat energy by friction. The heat energy raises the temperature of lead sheet. No reverse transformation of heat energy occurs.

(ii) The sudden and fast stretching of a spring may produce vibrations in it. Now a part of the energy is dissipated. This is the case of irreversible process.

(iii) Sudden expansion or contraction and rapid evaporation or condensation are examples of irreversible processes.

(iv) Produced by the passage of an electric current through a resistance is irreversible.

(v) Heat transfer between bodies at different temperatures is also irreversible.

(vi) Joule-Thomson effect is irreversible because on reversing the flow of gas a similar cooling or heating effect is not observed.

## Mixed Graphical Representation

### (1) PV-graphs

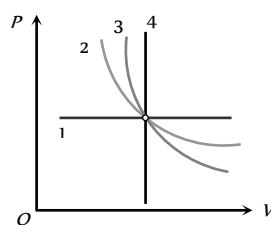


Fig. 14.26

1 → Isobaric ( $P$ -constant)

2 → Isothermal (Because  $P \propto \frac{1}{V}$ )

3 → Adiabatic (Because  $P \propto \frac{1}{V^\gamma}$ )

4 → Isochoric ( $V$ -constant)

### (2) PT-graphs

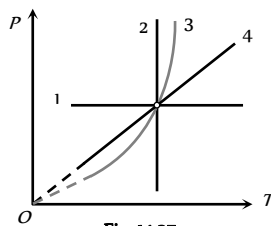


Fig. 14.27

1 → Isobaric ( $P$ -constant)

2 → Isothermal ( $T$ -constant)

3 → Adiabatic (Because  $P \propto T^{\frac{\gamma}{\gamma-1}}$ )

4 → Isochoric (In isochoric  $P \propto T$ )

### (3) VT-graphs

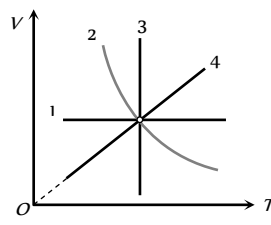


Fig. 14.28

1 → Isochoric ( $V$ -constant)

2 → Adiabatic (Because  $V \propto T^{\frac{1}{1-\gamma}}$ )

3 → Isothermal ( $T$ -constant)

4 → Isobaric (In isobaric  $V \propto T$ )

## Heat Engine

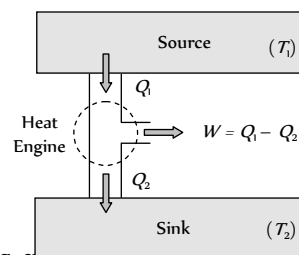
Heat engine is a device which converts heat into work continuously through a cyclic process.

The essential parts of a heat engine are

(1) **Source** : It is a reservoir of heat at high temperature and infinite thermal capacity. Any amount of heat can be extracted from it.

(2) **Working substance** : Steam, petrol etc.

(3) **Sink** : It is a reservoir of heat at low temperature and infinite thermal capacity. Any amount of heat can be given to the sink.



The working substance absorbs heat  $Q_1$  from the source, does an amount of work  $W$ , returns the same amount of heat to the sink and

Fig. 14.29

comes back to its original state and there occurs no change in its internal energy.

By repeating the same cycle over and over again, work is continuously obtained.

The performance of heat engine is expressed by means of “efficiency”  $\eta$  which is defined as the ratio of useful work obtained from the engine to the heat supplied to it.

$$\eta = \frac{\text{Work done}}{\text{Heat input}} = \frac{W}{Q_1}$$

For cyclic process  $\Delta U = 0$  hence from FLOT  $\Delta Q = \Delta W$

$$\text{So } W = Q_1 - Q_2 \Rightarrow \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

A perfect heat engine is one which converts all heat into work *i.e.*  $W = Q_1$  so that  $Q_2 = 0$  and hence  $\eta = 1$ .

But practically efficiency of an engine is always less than 1.

## Refrigerator or Heat Pump

A refrigerator or heat pump is basically a heat engine run in reverse direction.

It essentially consists of three parts

- (1) **Source** : At higher temperature  $T_1$ .
- (2) **Working substance** : It is called refrigerant liquid ammonia and freon works as a working substance.
- (3) **Sink** : At lower temperature  $T_2$ .

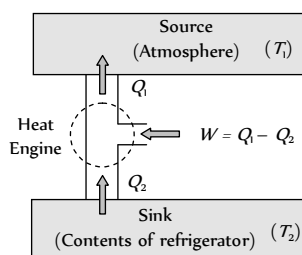


Fig. 14.30

The working substance takes heat  $Q_2$  from a sink (contents of refrigerator) at lower temperature, has a net amount of work done  $W$  on it by an external agent (usually compressor of refrigerator) and gives out a larger amount of heat  $Q_1$  to a hot body at temperature  $T_1$  (usually atmosphere). Thus, it transfers heat from a cold to a hot body at the expense of mechanical energy supplied to it by an external agent. The cold body is thus cooled more and more.

The performance of a refrigerator is expressed by means of “coefficient of performance”  $\beta$  which is defined as the ratio of the heat extracted from the cold body to the work needed to transfer it to the hot body.

$$\text{i.e. } \beta = \frac{\text{Heat extracted}}{\text{Work done}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

A perfect refrigerator is one which transfers heat from cold to hot body without doing work

$$\text{i.e. } W = 0 \text{ so that } Q_1 = Q_2 \text{ and hence } \beta = \infty$$

- (1) **Carnot refrigerator** : For Carnot refrigerator  $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

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

$$\text{So coefficient of performance } \beta = \frac{T_2}{T_1 - T_2}$$

where  $T_1$  = temperature of surrounding,  $T_2$  = temperature of cold body. It is clear that  $\beta = 0$  when  $T_2 = 0$

*i.e.* the coefficient of performance will be zero if the cold body is at the temperature equal to absolute zero.

(2) **Relation between coefficient of performance and efficiency of refrigerator**

$$\text{We know } \beta = \frac{Q_2}{Q_1 - Q_2} = \frac{Q_2 / Q_1}{1 - Q_2 / Q_1} \quad \dots (i)$$

$$\text{But the efficiency } \eta = 1 - \frac{Q_2}{Q_1} \text{ or } \frac{Q_2}{Q_1} = 1 - \eta \quad \dots (ii)$$

$$\text{From (i) and (ii) we get, } \beta = \frac{1 - \eta}{\eta}$$

## Second Law of Thermodynamics

First law of thermodynamics merely explains the equivalence of work and heat. It does not explain why heat flows from bodies at higher temperatures to those at lower temperatures. It cannot tell us why the converse is possible. It cannot explain why the efficiency of a heat engine is always less than unity. It is also unable to explain why cool water on stirring gets hotter whereas there is no such effect on stirring warm water in a beaker. Second law of thermodynamics provides answers to these questions. Statement of this law is as follows

(1) **Clausius statement** : It is impossible for a self acting machine to transfer heat from a colder body to a hotter one without the aid of an external agency.

From Clausius statement it is clear that heat cannot flow from a body at low temperature to one at higher temperature unless work is done by an external agency. This statement is in fair agreement with our experiences in different branches of physics. For example, electrical current cannot flow from a conductor at lower electrostatic potential to that at higher potential unless an external work is done. Similarly, a body at a lower gravitational potential level cannot move up to higher level without work done by an external agency.

(2) **Kelvin's statement** : It is impossible for a body or system to perform continuous work by cooling it to a temperature lower than the temperature of the coldest one of its surroundings. A Carnot engine cannot work if the source and sink are at the same temperature because work done by the engine will result into cooling the source and heating the surroundings more and more.

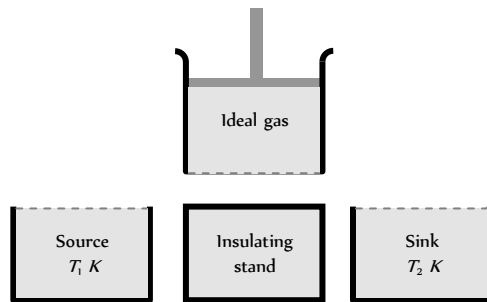
(3) **Kelvin-Planck's statement** : It is impossible to design an engine that extracts heat and fully utilises into work without producing any other effect.

From this statement it is clear that any amount of heat can never be converted completely into work. It is essential for an engine to return some amount of heat to the sink. An engine essentially requires a source as well as sink. The efficiency of an engine is always less than unity because heat cannot be fully converted into work.

## Carnot Engine



(i) Carnot designed a theoretical engine which is free from all the defects of a practical engine. This engine cannot be realised in actual practice, however, this can be taken as a standard against which the performance of an actual engine can be judged.



It consists of the following parts  
Fig. 14.31

(i) A cylinder with perfectly non-conducting walls and a perfectly conducting base containing a perfect gas as working substance and fitted with a non-conducting frictionless piston

(ii) A source of infinite thermal capacity maintained at constant higher temperature  $T_1$

(iii) A sink of infinite thermal capacity maintained at constant lower temperature  $T_2$

(iv) A perfectly non-conducting stand for the cylinder.

(2) **Carnot cycle** : As the engine works, the working substance of the engine undergoes a cycle known as Carnot cycle. The Carnot cycle consists of the following four strokes

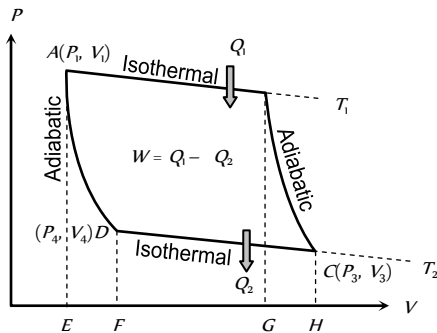


Fig. 14.32

(i) First stroke (Isothermal expansion) (curve AB) :

The cylinder containing ideal gas as working substance allowed to expand slowly at this constant temperature  $T_1$ .

Work done = Heat absorbed by the system

$$W_1 = Q_1 = \int_{V_1}^{V_2} P dV = RT_1 \log_e \left( \frac{V_2}{V_1} \right) = \text{Area ABGE}$$

(ii) Second stroke (Adiabatic expansion) (curve BC) :

The cylinder is then placed on the non conducting stand and the gas is allowed to expand adiabatically till the temperature falls from  $T_1$  to  $T_2$ .

$$W_2 = \int_{V_2}^{V_3} P dV = \frac{R}{(\gamma - 1)} [T_1 - T_2] = \text{Area BCHG}$$

(iii) Third stroke (Isothermal compression) (curve CD) :

The cylinder is placed on the sink and the gas is compressed at constant temperature  $T_2$ .

Work done = Heat released by the system

$$W_3 = Q_2 = - \int_{V_3}^{V_4} P dV = -RT_2 \log_e \frac{V_4}{V_3}$$

$$= RT_2 \log_e \frac{V_3}{V_4} = \text{Area CDFH}$$

(iv) Fourth stroke (adiabatic compression) (curve DA) : Finally the cylinder is again placed on non-conducting stand and the compression is continued so that gas returns to its initial stage.

$$W_4 = - \int_{V_4}^{V_1} P dV = - \frac{R}{\gamma - 1} (T_2 - T_1) = \frac{R}{\gamma - 1} (T_1 - T_2) = \text{Area ADFE}$$

(3) **Efficiency of Carnot cycle** : The efficiency of engine is defined as the ratio of work done to the heat supplied i.e.

$$\eta = \frac{\text{Work done}}{\text{Heat input}} = \frac{W}{Q_1}$$

Net work done during the complete cycle

$$W = W_1 + W_2 + (-W_3) + (-W_4) = W_1 - W_3 = \text{Area ABCD}$$

$$[\text{As } W_2 = W_4]$$

$$\therefore \eta = \frac{W}{Q_1} = \frac{W_1 - W_3}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{W_3}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$\text{or } \eta = 1 - \frac{RT_2 \log_e (V_3 / V_4)}{RT_1 \log_e (V_2 / V_1)}$$

Since points B and C lie on same adiabatic curve

$$\therefore T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \text{ or } \frac{T_1}{T_2} = \left( \frac{V_3}{V_2} \right)^{\gamma-1} \quad \dots(i)$$

Also point D and A lie on the same adiabatic curve

$$\therefore T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1} \text{ or } \frac{T_1}{T_2} = \left( \frac{V_4}{V_1} \right)^{\gamma-1} \quad \dots(ii)$$

$$\text{From (i) and (ii), } \frac{V_3}{V_2} = \frac{V_4}{V_1} \text{ or } \frac{V_3}{V_4} = \frac{V_2}{V_1} \Rightarrow \log_e \left( \frac{V_3}{V_4} \right) = \log_e \left( \frac{V_2}{V_1} \right)$$

$$\text{So efficiency of Carnot engine } \eta = 1 - \frac{T_2}{T_1}$$

(i) Efficiency of a heat engine depends only on temperatures of source and sink and is independent of all other factors.

(ii) All reversible heat engines working between same temperatures are equally efficient and no heat engine can be more efficient than Carnot engine (as it is ideal).

(iii) As on Kelvin scale, temperature can never be negative (as 0 K is defined as the lowest possible temperature) and  $T_1$  and  $T_2$  are finite, efficiency of a heat engine is always lesser than unity, i.e., whole of heat can never be converted into work which is in accordance with second law.

(4) **Carnot theorem** : The efficiency of Carnot's heat engine depends only on the temperature of source ( $T$ ) and temperature of sink ( $T_2$ ), i.e.,

$$\eta = 1 - \frac{T_2}{T_1}$$

Carnot stated that no heat engine working between two given temperatures of source and sink can be more efficient than a perfectly reversible engine (Carnot engine) working between the same two

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temperatures. Carnot's reversible engine working between two given temperatures is considered to be the most efficient engine.

**Table 14.3 : Difference Between Petrol Engine and Diesel Engine**

Petrol engine	Diesel engine
Working substance is a mixture of petrol vapour and air.	Working substance in this engine is a mixture of diesel vapour and air.
Efficiency is smaller (~47%).	Efficiency is larger (~55%).
It works with a spark plug.	It works with an oil plug.
It is associated with the risk of explosion, because petrol vapour and air is compressed. So, low compression ratio is kept.	No risk of explosion, because only air is compressed. Hence compression ratio is kept large.
Petrol vapour and air is created with spark plug.	Spray of diesel is obtained through the jet.

## Entropy

Entropy is a measure of disorder of molecular motion of a system. Greater is the disorder, greater is the entropy.

The change in entropy *i.e.*

$$dS = \frac{\text{Heat absorbed by system}}{\text{Absolute temperature}} \text{ or } dS = \frac{dQ}{T}$$

The relation is called the mathematical form of Second Law of Thermodynamics.

(1) **For solids and liquids**

(i) When heat given to a substance changes its state at constant temperature, then change in entropy  $dS = \frac{dQ}{T} = \pm \frac{mL}{T}$

where positive sign refers to heat absorption and negative sign to heat evolution.

(ii) When heat given to a substance raises its temperature from  $T_1$  to  $T_2$ , then change in entropy

$$dS = \int \frac{dQ}{T} = \int_{T_1}^{T_2} mc \frac{dT}{T} = mc \log_e \left( \frac{T_2}{T_1} \right)$$

$$\Rightarrow \Delta S = 2.303 mc \log_{10} \left( \frac{T_2}{T_1} \right)$$

(2) **For a perfect gas :** Perfect gas equation for  $n$  moles is  $PV = nRT$

$$\Delta S = \int \frac{dQ}{T} = \int \frac{\mu C_V dT + P dV}{T} \quad [\text{As } dQ = dU + dW]$$

$$\Rightarrow \Delta S = \int \frac{\mu C_V dT + \frac{\mu RT}{V} dV}{T} \quad [\text{As } PV = \mu RT]$$

$$= \mu C_V \int_{T_1}^{T_2} \frac{dT}{T} + \mu R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\therefore \Delta S = \mu C_V \log_e \left( \frac{T_2}{T_1} \right) + \mu R \log_e \left( \frac{V_2}{V_1} \right)$$

$$\text{In terms of } T \text{ and } P, \Delta S = \mu C_P \log_e \left( \frac{T_2}{T_1} \right) - \mu R \log_e \left( \frac{P_2}{P_1} \right)$$

$$\text{and in terms of } P \text{ and } V, \Delta S = \mu C_V \log_e \left( \frac{P_2}{P_1} \right) + \mu C_P \log_e \left( \frac{V_2}{V_1} \right)$$

✍ When a thermos bottle is vigorously shaken :

Heat transferred to the coffee  $\Rightarrow \Delta Q = 0$

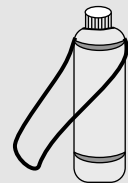
[As thermos flask is insulated from the surrounding]

Work is done on the coffee against viscous force

$\Delta W = (-)$

Internal energy of the coffee increases  $\Delta U = (+)$

and temperature of the coffee also increases  $\Delta T = (+)$



✍ **Work done without the volume limits**

$$W = \int_{V_i}^{V_f} P dV$$

From this equation it seems as if work done can be calculated only when  $P$ - $V$  equation is known and limits  $V_i$  and  $V_f$  are known to us. But it is not so. We can calculate work done if we know the limits of temperature.

For  $\mu$  moles of an ideal gas if  $P = \frac{\alpha}{T}$  with temperature limits  $T_1$  and  $2T_1$ ,

$$\text{From } PV = \mu RT \Rightarrow V = \frac{\mu RT}{P} = \frac{\mu RT^2}{\alpha} \Rightarrow dV = \frac{2\mu RT}{\alpha} dT$$

$$\therefore W = \int_{V_i}^{V_f} P dV = \int_{T_0}^{2T_0} \left( \frac{\alpha}{T} \right) \left( \frac{2\mu RT}{\alpha} \right) dT = 2\mu RT_0$$

✍ **Work done with spring :** If mass less piston is attached to a spring of force constant  $K$  and a mass  $m$  is placed over the piston. If the external pressure is  $P_0$  and due to expansion of gas the piston moves up through a distance  $x$  then

Total work done by the gas

$$W = W_1 + W_2 + W_3$$

where  $W_1$  = Work done against

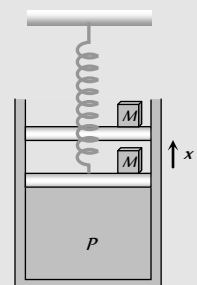
external pressure ( $P_0$ )

$W_2$  = Work done against spring

force ( $Kx$ )

$W_3$  = Work done against gravitational force ( $mg$ )

$$\therefore W = P_0 V + \frac{1}{2} Kx^2 + mgx$$



✍ The efficiency of an actual engine is much lesser than that of an ideal engine. Actually the practical efficiency of a steam engine is about (8-15)% while that of a petrol engine is 40%. The efficiency of a diesel engine is maximum and is about (50-55)%.

✍ When  $P$  and  $V$  bear the relation  $PV^\gamma = \text{constant}$ , where  $\gamma \neq 1$  or  $\gamma$  the process is called a polytropic one. In this process the molar heat

capacity is,  $C = C_V + \frac{R}{1-\gamma} = \frac{R}{\gamma-1} + \frac{R}{1-\gamma}$

✍ **Enthalpy :** Four quantities called "thermodynamic potentials" are useful in the chemical thermodynamics of reactions and non-cyclic processes. They are internal energy, the enthalpy, the Helmholtz free energy and the Gibbs free energy. Enthalpy is defined by

# Tips & Tricks

$$H = U + PV$$

where  $P$  and  $V$  are the pressure and volume, and  $U$  is internal energy, Enthalpy is somewhat parallel to the first law of thermodynamics for a constant pressure system  $Q = \Delta U + P\Delta V$  since in this case  $Q = \Delta H$ .

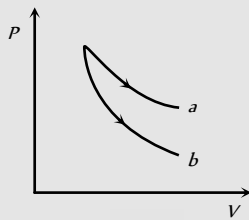
### ✍ Confusion about FLOT

It is typical for chemistry texts to write the first law as

$$\Delta U = \Delta Q + \Delta W$$

It is the same law, of course the thermodynamic expression of the conservation of energy principle. It is just that  $W$  is defined as the work done on the system instead of work done by the system. In the context of physics, the common scenario is one of adding heat to a volume of gas and using the expansion of that gas to do work, as in the pushing down of a piston in an internal combustion engine. In the context of chemical reactions and process, it may be more common to deal with situations where work is done on the system rather than by it.

### ✍ Possibilities



If  $a \longrightarrow$  Isothermal then  $b \longrightarrow$  Must be adiabatic

But If  $b \longrightarrow$  adiabatic then it is not compulsory that  $a$  must be isothermal, it may be adiabatic also.