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Introductory Thermodynamic Concepts

1.1. Thermodynamic System. *A thermodynamic system may be defined simply as region in space or control volume or quantity of matter upon which attention is focused for study.*

1.2. State. The state of a system is its condition or configuration, described in sufficient detail so that one state may be distinguished from all other states. The state may be identified by certain observable macroscopic properties, some familiar such properties being, pressure, temperature, density etc.

1.3. Property. A property of a system is any observable characteristic of a system. The properties we shall deal with are measurable in terms of numbers and units of measurements, and include such physical quantities as location, speed, pressure, density etc. A listing of a sufficient number of independent properties costitute a complete definition of the state of a system. Such characteristics are also called state variables or thermodynamic co-ordinates of the system.

When all the properties of a system have definite values, the system is said to be in a definite state. Systems in identical states must have identical values of their corresponding properties. *Thus property of the system depends solely upon the state of the system and not upon how that state may have been reached.*

1.4. Intensive and Extensive Properties. An intensive property of a system is one whose value does not depend upon the mass of the system. Such properties include temperature, pressure, density and specific volume. Whatever may be mass of the system they are the same for the entire system.

An extensive property of the system is dependent on the mass of the system. It is, in fact, proportional to the mass of the system. Volume is an extensive property.

1.5. Specific Weight. It is also known as the weight density. It is the weight per unit volume. It may be expressed in $\frac{\text{Newton}}{\text{m}^3}$ and depends upon both the density of the substance and the value of the gravitational acceleration g. Let w represent the weight corresponding to certain mass m ; then

$$w = \frac{1}{g_c} . mg$$

where g_c is the constant of proportionality and its numerical value is the value for standard acceleration due to gravity in MKS units and 1 in SI units.

If both sides of this equation are divided by volume, then

$$w_s = \rho \frac{g}{g_c} \qquad \text{...(1.1)}$$

where w_s is the weight density and ρ is the mass density. For example, if the density of water at 22°C is 1000 kg/m^3, its specific weight is

$$w_s = \frac{1000}{g_c} . g.$$

Specific weight is the same numerically as the density only if the local acceleration g is numerically equal to the dimensional constant g_c. It may be noted that w_s is the force per unit volume whereas ρ is the mass per unit volume. The units of g are m/sec^2. The units of g_c are kgm/kgf sec^2 in MKS units and kgm/N sec^2 in SI units. In MKS units $g_c \simeq 9.81 \frac{\text{kgm}}{\text{kgf sec}^2}$ and in SI units $g_c = 1$ kgm/N sec^2. Thus in SI units $w_s = \rho g = \text{N/m}^3$ where ρ is expressed in kg/m^3.

1.6. Specific Volume. It is defined as the volume per unit mass and may be expressed in m^3/kg. It is reciprocal of the density

$$v = \frac{1}{\rho}$$

where v is the specific volume.

1.7. Pressure. The pressure exerted by a system is the force exerted normal to a unit area of the boundary. When a fluid is contained within a vessel, the pressure exerted on the vessel is equal to the mean change of momentum of the molecules exerted perpendicular to the confining boundary per unit area and per unit time

$$p = \lim_{\Delta A \to \Delta A'} \frac{\Delta F_n}{\Delta A} \qquad \text{...(1.2)}$$

where ΔF_n is the force normal to the area ΔA,

$\Delta A'$ is the smallest possible area capable of maintaining a continuum.

Consider a homogeneous fluid of density ρ in static equilibrium. A pressure difference exists between two points which are separated by distance h in the vertical directions. The weight of a cylinder of fluid can be equated to the difference between forces due to pressure at two ends of the cylinder so that fundamental relationship is

$$\Delta pA = w_g pA$$

or

$$\Delta p = w_g p = \rho gh \qquad \text{...(1.3)}$$

Table 1. Conversion Factors for Pressure

	bar	*dyne/cm^2*	*kgf/cm^2 ata*	*N/m^2 or Pa*	*mm Hg (21°C)*	*mm H_2O (21°C)*	*atm*
bar =	1	10^6	1.01972	10^5	750.062	10197.2	0.986923
1 dyne/cm^2 =	10^{-6}	1	101.972×10^{-8}	0.1	750.062×10^{-6}	10197.2×10^{-6}	0.986923×10^{-6}
1 kgf/cm^2 or ata =	0.980665	0.980665×10^6	1	0.980665×10^5	735.559	10000	0.967838×10^{-5}
N/m^2 or Pa =	10^{-5}	10	10.1972×10^{-6}	1	750.062×10^{-5}	10197.2×10^{-5}	0.986923×10^{-5}
1 mm Hg (21°C) =	1.333223×10^{-3}	1333.223	10.3595 10^{-2}	133.3223	1	13.5951	1.31578×10^{-3}
1 mm H_2O (21°C) =	98.0665×10^{-6}	98.0665	10^{-4}	9.80665	0.073556	1	96.7838×10^{-6}
1 atm =	1.01325	101.325×10^4	1.03323	101325	760	10332.276	1

1.8. Thermodynamic Co-ordinates. The thermodynamic properties used for locating thermodyamic state point are defined as thermodynamic co-ordinates.

1.9. Equilibrium. When an isolated system is left to itself, all its properties, like pressure, elastic stress etc. may change with time but eventually these changes will cease when the system will be said to be in mechanical equilibrium. This, however, does not mean that the pressure is the same at all points A vertical column of fluid will be in mechanical equilibrium with different pressures as different elevations of the fluid column.

In thermodynamics, it is imperative to take into account more than purely mechanical equilibrium of a system. If there are variations of temperature from point to point of an isolated system, these should cease, so that the system comes to what is called thermal equilibrium.

Finally, suppose the system contains substances that can react chemically. All the chemical reactions will cease and eventually a chemical equilibrium will result. *Thus a system in mechanical thermal and chemical equilibrium is said to be in thermodynamic equilibrium.*

1.10. Path. If the thermodynamic system passes through a series of states, it is said to describe a path.

1.11. Process. Whenever a change of state takes place, process is the cause. The thermodynamic process consists of enough information about the thermodynamic co-ordinates at successive state points in thermodynamic equilibrium to be able to plot a path of the change of state on the thermodynamic plane.

1.12. Cyclic Process. If we start with a particular set of thermodynamic co-ordinates of a system describing its state point and then carry the process through a complete cycle ending up with the initial state point, the system is said to undergo a cyclic process. Thus all the thermodynamic properties are the same at the start and end of a cyclic process.

1.13. Quasi-static Process. If a process is carried out it such a way that at every instant the system departs only infinitesimally from the thermodynamic equilibrium state, such a process is defined as Quasi-static process *i.e.* a process closely approximating a succession of equilibrium states is known as quasi-static process. Only a quasi-static process can be represented on a thermodynamic plane. Referring to Fig. 1.1. *AB* is a quasi-static process and at the successive states for example at 1, 2, 3 etc. the system is very nearly in thermodynamic equilibrium.

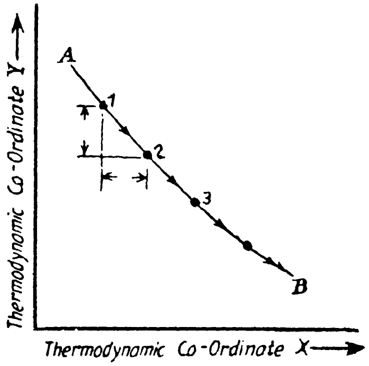


Fig. 1.1

1.14. Energy. Simplest definition of Energy is "capacity for producing an effect". It can be classified as (*i*) stored energy which is contained within the system boundaries and (*ii*) energy in transmission which crosses the system boundaries. Examples of stored energy are : (*i*) Potential energy, (*ii*) Kinetic energy, (*iii*) Internal energy etc. Examples of energy in transition are : (*i*) Heat, (*ii*) Work, (*ii*) Electrical energy etc.

1.15. Potential Energy. Potential energy is the energy contained in the system by virtue of its elevation with reference to an arbitrary chosen datum usually the sea level. Or alternatively it is equivalent to energy required to raise the system from an arbitrary datum usually the sea level.

If F = Force exerted by the system of mass m where the local acceleration due to gravity is g.

We have $F \propto m.g = mg$

If Z = the total distance through which system is raised.

$$\text{Potential energy (P.E.)} = \int_0^Z F dZ = \int_0^Z m\, g dZ$$

$$= \mathbf{m.\, gZ} \qquad \text{...(1.4)}$$

1.16. Kinetic Energy. Energy possessed by a system by virtue of its motion as a whole is called Kinetic Energy. Alternatively, it is the energy that could be recovered when the system is brought to stagnation state in the absence of friction.

We have $F = m.\dfrac{dV}{dt}$

and $F\,dx = m.\dfrac{dV}{dt}.\,dx = m\,.\dfrac{dx}{dt}.\,dV$

or $\text{Work} = \int_0^V F dx = \int_0^V m.\dfrac{dx}{dt}\,dV$

$$= \text{Kinetic energy}$$

$$= \int_0^V m\,V\,dV = \left[\frac{m}{2}V^2\right]_0^V$$

Thus $\text{K.E.} = \dfrac{1}{2} m\,V^2$ ...(1.5)

1.17. Work. In thermodynamics, work is defined as the energy in transition. A definition for work which would allow for all forms of work including mechanical work may be given as follows :

"Work is transferred from the system during a given operation if the sole effect external to the system can be reduced to the rise of a weight."

1.18. Work Done During a Quasi-static Process. There are various ways of work done by the system like work done by rotating shafts, electrical work, work done by displacement of the boundary of the system, as in piston cylinder arrangement. Prior to this, no specific mention was made to how the system co- ordinates changed. In this section a piston and cylinder arrangement is taken and the work done at the moving system boundaries during a quasi-static process is considered. A technically important phenomenon in many engineering processes is one in which work is done *by* the system by the expansion of gases in a piston and cylinder arrangement and work is done *on* the system by compression process. The piston moves along the cylinder and exerts a progressively varying pressure on the fluid and for a small displacement *dx* of the piston, the process may be considered quasi-static. Refer Fig. 1.2.

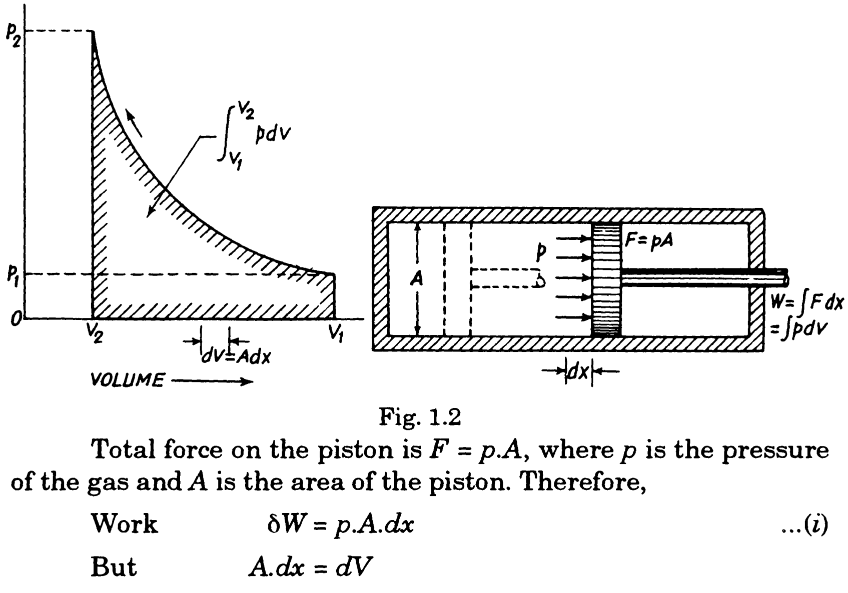


Fig. 1.2

Total force on the piston is $F = p.A$, where p is the pressure of the gas and A is the area of the piston. Therefore,

Work $\delta W = p.A.dx$ ...(*i*)

But $A.dx = dV$

Therefore, $\delta W = p.dV$ ...(*ii*)

The work done at the moving system boundaries can be calculated by integrating equation (*ii*). But the integration can be done only if the relationship between p and V is known during the process. This relationship may be known in the form of a graph as shown in Fig. 1.2 or by an equation. Consider the graph in Fig. 1.2 which shows a quasi-static compression process. Thus, each point on the process 1-2 represents a definite state and these states will correspond to the actual states of the system only if there is infinitesimal departure from the thermodynamic equilibrium. Thus

Work done *on* the system

$$ {}_1W_2 = \int_1^2 \delta W = \int_{V_1}^{V_2} pdV \qquad \text{...(1.6)}$$

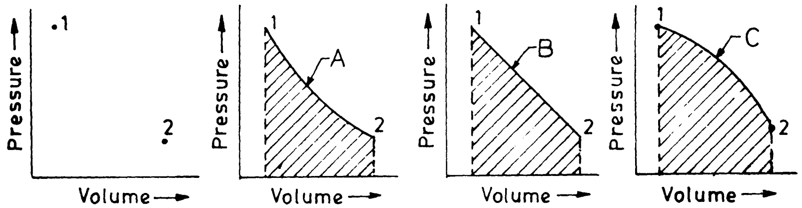
And it is clear that the work done during this quasi-static process is the area under the curve shown hatched in Fig. 1.2.

If the process was carried out from V_2 to V_1, *i.e.*, from 2 to 1, it would be an expansion process and the work will be done *by* the system in that case. Work done *by* the system is considered positive and work done *on* the system is considered negative. It is very important to note that the system considered is a closed non-flow one. Thus $\int pdV$ is the work done during a quasi-static process of only a non-flow system. For unit mass it can be written as $\int pdv$, where v is the specific volume.

1.19. PdV Work, a Path Function. Refer Fig. 1.3 (*a*), (*b*), (*c*) and (*d*). Since many problems in thermodynamics involve the use of the equation

$$\delta W = p.dV$$

it is convenient to represent equation $\delta W = p.dV$ graphically. Let us consider state 1 and state 2 as shown on the $p.V$ plane in Fig. 1.3 (*a*). It is possible to go from state 1 to state 2 by many different quasi-static paths as shown in Fig. 1.3 (*b*), (*c*) and (*d*). And since, ${}_1W_2 = \int_1^2 pdV$ = area under the curve, it is clear that amount of work done in each case is dependent on the path followed and not merely the end states. Thus work is called a path function. In general a quasi-static process may be represented by an equation of the from



(*a*) (*b*) (*c*) (*d*)

Fig. 1.3

pV^n = constant, where the index n may have a value from $-\propto$ to $+\propto$. Such a process is often called polytropic process. Fig. 1.4 shows a few typical cases of the polytropic process. For $n = 0$ we have $pV^0 = p$ = constant (Isobaric process) for $n = 1$, we have

pV = constant (Isothermal process) and for $n = \propto$, we have $p^{1/\propto}\ V = p^{\circ}V = V$ = constant (Isometric process).

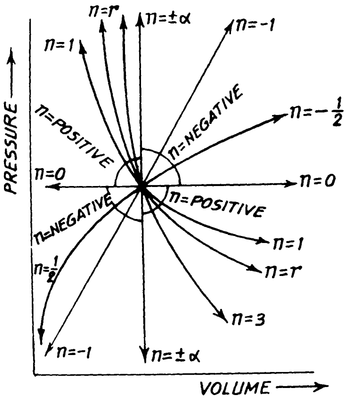


Fig. 1.4

1.20. Limitations to the use of $\int$ pdv

For $\int pdv$ to represent work per unit mass following conditions must be satisfied :

(*i*) The system is a closed one and the process takes place in a non-flow system.

(*ii*) The process is Quasi-static. Such a process is often referred to as reversible process since a quasi-static expansion process according to a particular p-v relationship between two states can be reversed as quasi-static compression process according to the same p-v relationship between the same states.

(*iii*) The boundary of the system should move in order that work may be transferred.

All the conditions must be simultaneously satisfied to allow the use of equation $\int \delta W = \int pdv$.

1.21. Flow Work.

Refer Fig. 1.5. A further form of energy in transition as work is invariably associated with the mere fact of the maintenance of the flow of fluid along a channel, or its introduction into any region against the pressure then

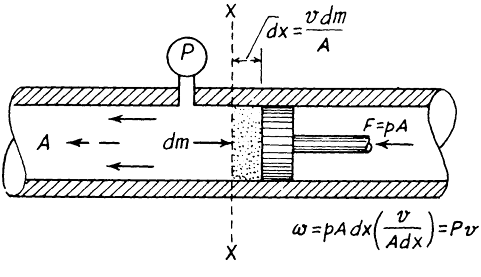


Fig. 1.5

existing in the fluid or region. The concept might be developed by reference to Fig. 1.5. Here the boundaries for the system, *i.e.* the stream (of transverse A) are represented by the solid horizontal lines and section line XX' ; the other boundary of the stream to the left is not shown. A particular mass dm of the fluid is represented as about to pass along the channel past the boundary XX' and into the region to the left of it. The mass dm has volume dV. Therefore the specific volume of the fluid v

$$v = \frac{dV}{dm}$$

and absolute pressure p exists at section XX'. The moving piston which may be regarded as real or in fact as formed by the fluid to the right of the mass dm, is the agency by which flow is maintained.

For affecting the entry of the fluid of mass dm and volume dV into the region, a force pA must have acted through a distance dx, where

$$dx = \frac{dV}{A} \qquad \text{...(1.7)}$$

Defining as flow work, the mechanical work so required for affecting entry of the mass into the region, the amount of such work per unit mass fluid entering becomes

$$w_{flow} \text{ (per unit mass)} = \frac{p\,Adx}{dm} \qquad \text{...(1.8)}$$

$$= \frac{(pA)\,dV/A}{dm} = p\,\frac{dV}{dm}$$

$$= pv \qquad \text{...(1.9)}$$

Comments on Flow Work

(*i*) The magnitude of the flow work per unit mass of fluid is uniquely expressible by the simple product of the two properties of the fluid, pressure and specific volume.

(*ii*) This product may, however, be assigned energy significance only in association of the flow phenomenon and in the flow energy significance that has been indicated.

(*iii*) The item is not a measure of the energy that has been required for prior compression of the fluid to the existing pressure, and is independent of any energy that may have been required to give the fluid a velocity. Instead it relates solely to the work that in some manner must be furnished for affecting the advance of the fluid against the restraining pressure during that advance.

1.22. Heat. When two systems originally at different temperatures are brought into contact such that the mass flow across the boundary does not take place, but energy transfer can take place, it is shown by common experience the these two systems come to the equilibrium and reach a temperature common to both, and that temperature is in between the two original temperatures of the systems. Thus the systems have influenced each other. This influence has passed from system at higher temperature to system at lower temperature, or we say that heat has transferred from system at higher temperature to system at lower temperature by virtue of temperature difference. It is the energy in transition and is not property. Heat will be denoted Q. Its units are Joule abbreviated as J.

Heat flow rate is expressed as Watt or J/sec.

1.23. Specific Heat. The heat required by a unit mass of a substance to rise temperature by one degree is called the specific heat of the substance. It is also called the heat capacity of the substance.

If C_n = specific heat of substance
δq = heat added to unit mass
dt = rise in temperature.

We have

$$C_p = \lim_{\Delta t \to 0} \frac{\Delta Q}{m\Delta t} = \lim_{\Delta t \to 0} \frac{\Delta q}{\Delta t} = \frac{\delta q}{dt}$$

or $$\delta q = C_n\, dt$$

or $$\delta Q = mC_n\, dt \qquad \text{...(1.10)}$$

$$\therefore \quad {}_1Q_2 = \int_1^2 mC_n\, dt \qquad \text{...(1.11)}$$

Thus C_n is the specific heat when the heat is transferred to the system undergoing a general process or polytropic process. Two special cases of significance are when heat is transferred during constant volume process and during constant pressure process.

Speific heat $C_p = \left(\frac{\delta q}{\delta t}\right)_p$ at constant pressure

and specific heat $C_v = \left(\frac{\delta q}{\delta t}\right)_v$ at constant volume ...(1.13)

Units for specific heat follow from the definition, *i.e.* $\frac{\text{J}}{\text{kg}^\circ\,\text{K}}$.

1.24. Perfect Gas. A perfect gas strictly obeys all the gas laws under all conditions of pressure and temperature. In this sense no gas which exists in nature is perfect. But this definition applies fairly well to some gases within the range of pressure and temperature met with in applied thermodynamics. Examples are, air and nitrogen. Thus these gases may be considered as perfect. They are also called ideal gases.

1.25. Law I—Boyle's Law. *The volume of a given mass of a perfect gas varies inversely as the absolute pressure when temperature is constant.*

Let p be the absolute pressure of the gas
v be the specific volume of the gas at pressure p
T be the absolute temperature of the gas.

$$\therefore \quad v \propto \frac{1}{p} \text{ when } T \text{ is constant}$$

$$pv = \text{constant} = C \qquad \text{...(1.14)}$$

where C is the constant of proportionality.

1.26. Law II—Charles Law. *The volume of a given mass of a gas varies directly as its absolute temperature, if the pressure remains unchanged.*

Let p be the absolute pressure
v be the specific volume of gas
T be the absolute temperature.

Therefore, $v \propto T$ when p is constant

$$\text{or} \quad \frac{v}{T} = \text{constant} \qquad \text{....(1.15)}$$

1.27. Characteristic Equation of Gas. In engineering practice, volume, pressure, and temperature, all very simultaneously and therefore, Boyle's Law or only Charles' Law is not applicable. But from both these laws a general equation for a mass of gas undergoing changes in temperature, pressure and volume can be obtained.

$$v \propto \frac{1}{p} \text{ when } T \text{ is constant} \qquad \text{... Boyle's Law}$$

$$v \propto T \text{ when } p \text{ is constant} \qquad \text{... Charles' Law}$$

$$\therefore \quad v \propto \frac{T}{p} \text{ when } T \text{ and } p \text{ both vary}$$

$$\text{or} \quad v = k\frac{T}{p}$$

where k is a constant and depends upon the scale of temperature used and the properties of gas.

$$\text{or} \quad pv = RT \text{ for unit mass}$$

and $$V = mR\frac{T}{p}$$

where m is the mass of gas, and R is a constant depending upon the temperature scale and properties of gas

i.e. $$pV = mRT \qquad \text{...(1.16)}$$

where R is called the characteristic gas constant and equation (1.16) is called the. characteristic equation of a gas.

In order to find out the units of the gas constant R,

let p = Absolute pressure of gas in N per sq metre *i.e.* $\frac{\text{N}}{\text{m}^2}$

V = Volume of gas in cubic metre *i.e.* m^3

m = Mass of gas in kg

T = Absolute temperature of gas in °K

$$\therefore \quad R = \frac{pV}{mT} = \frac{\text{N} \times \text{m}^3}{\text{m}^2 \times \text{kg} \times {}^\circ\text{K}}$$

$$= \text{Nm per kg per } {}^\circ\text{K or J/kg } {}^\circ\text{K}$$

R = 287 J/kg °K for air

= 4124.6 J/kg °K for H_2

= 296.8 J/kg °K for N_2

= 259.8 J/kg °K for O_2.

1.28. Universal Gas Constant. It is interesting to note that the product of the characteristic gas constant and the molecular weight of an ideal gas is a constant number. It is equal to 8314. Thus 8314 J/kg mol °K is called the universal gas constant. It is verified as under :

Molecular weight M		× *R*	= *MR*
For air	29	287	$\simeq$ 8324
for H_2	2.016	4124.6	$\simeq$ 8315
for N_2	28.016	296.8	$\simeq$ 8315
for O_2	32	259.8	$\simeq$ 8316

1.29. Law III—Avogadro's Law or Avogadro's Hypo thesis. *Avogadro's Law states that the molecular weights of all the perfect gases occupy the same volume under the same conditions of pressure and temperature.*

Experiment shows that average volume of one mol of the permanant gases is 22.4136 m^3 at standard atmospheric pressure 1 atm = 1.01325 bar) and 0°C.

Thus $$MR = \frac{1.01325 \times 10^5 \times 22.4136}{273.16}$$

$$= 8314.02 \simeq 8314 \text{ J/kg mol } {}^\circ\text{K}.$$

Since MR for all ideal gases is constant and is equal to 8314 J/kg mol °K it follows that the kg mol volume for all gases at N.T.P. is same. Same will hold good for S.T.P. or any specified conditions of pressure and temperature.

1.30. First Law of Thermodynamics. *Whenever a system undergoes a cyclic change, the algebraic sum of work transfers is proportional to the algebraic sum of heat transfers or work and heat are mutually convertible one into the other.*

1.31. Energy-Internal Energy. *There exists a property of a system called energy, E, such that change in its value is the algebraic sum of the heat supply and the work done during any change in state.*

Energy E may include many types of energies like kinetic energy, potential energy, electric energy, magnetic energy, surface tension, etc. but from thermodynamic point of view these energies are ignored and the energy due to rise in temperature alone is considered. It is called internal energy denoted by U in this book.

Thus
$$\Delta U = Q - W \qquad \text{...(1.17)}$$

or
$$U_2 - U_1 = \int_1^2 (\delta Q - \delta W) \qquad \text{...(1.18)}$$

1.32. Adiabatic Work. Neglecting potential energy, kinetic energy etc. it has been proved that

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

If the change of state stakes place adiabatically, *i.e.* without any heat transfer, the equation is modified as

$$\Delta U = W_{ad} \qquad \text{...(1.19)}$$

where W_{ad} is the adiabatic work.

It has been already established that between two states the change in internal energy ΔU is independent of the path followed for the change of state. Thus, it follows that adiabatic work W_{ad} has the same value for all adiabatic paths between the same pair of the end states.

Further, it may be noted that between the same pair of end states, the difference between the actual work and the adiabatic work is equal to heat transfer between the system and the surroundings. Thus

$$Q = W - W_{ad} \qquad \text{...(1.20)}$$

Problem 1.1. *Fig. 1.6 shows three quasi-static processes by which a gas may be taken from an equilibrium state 1 to a second equilibrium state 2. Path A is an adiabatic process. Path B consists* *of a process at constant volume followed by process at constant pressure and path C consists of a process at constant pressure followed by a process at constant volume. If internal energy at state 1 is 500 Nm, determine the internal energy at state 2 and the energy flowing into the system during these three paths when*

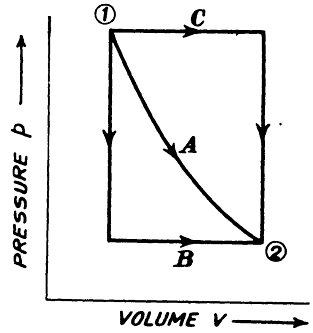


Fig. 1.6

$W_A = W_{ad} = 100\ Nm$

$W_B = 80\ Nm$

$W_C = 130\ Nm$

Solution. Path A, $Q = 0$.

Therefore $\Delta U = W_{ad}$

or $(U_1 - U_2) = W_{ad}$

i.e. $U_2 = U_1 - W_{ad} = 500 - 100 = 400$ Nm

Path B, $Q = (U_2 - U_1) + W_B = (400 - 500) + 80$

$= -20$ Nm

Thus 20 Nm of energy flows out from the system to the surroundings.

Path C, $Q = (U_2 - U_1) + W_C = (400 - 500) + 130$

$= 30$ Nm

Thus 30 Nm of energy flows into the system from the surroundings.

Problem 1.2. *A system (Fig. 1.7) is taken from state 1 to state 2 along the path 1-A-2. During the process, 280 kJ of heat flows into the system which in turn does 100 kJ of work. How much heat flows into the system if the path followed is 1-B-2 with 48 kJ of work done. The system is returned to state 1 by path 2-C-1 and 80 kJ of work is done on the system. Determine the heat transfer between the system and the surroundings.*

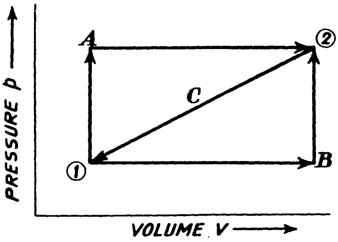


Fig. 1.7

Solution. For process 1-A-2,

$Q = \Delta U + W$

or $280 = \Delta U + 100.$

Therefore, $\Delta U = \mathbf{180\ kJ.}$

For process 1-*B*-2,

$$Q = \Delta U + W = 180 + 48 = \mathbf{228\ kJ.}$$

For process 2-*C*-1,

$$Q = \Delta U + W = -180 - 80 = \mathbf{-260\ kJ.}$$

1.32. First Law of Thermodynamics Analysis of Non-flow System. The purpose of the analysis is to apply the First Law of Thermodynamics to process in which a non-flow system changes from one state to the other, and to develop some useful relations.

(*i*) **Constant volume Process.** The equations for a process according to the First Law of Thermodynamics can be written as

$$_1Q_2 = {}_1W_2 + (U_2 - U_1).$$

Refer Fig. 1.8. It explains the constant volume process. Main characteristic of this process is that displacement work is eliminated.

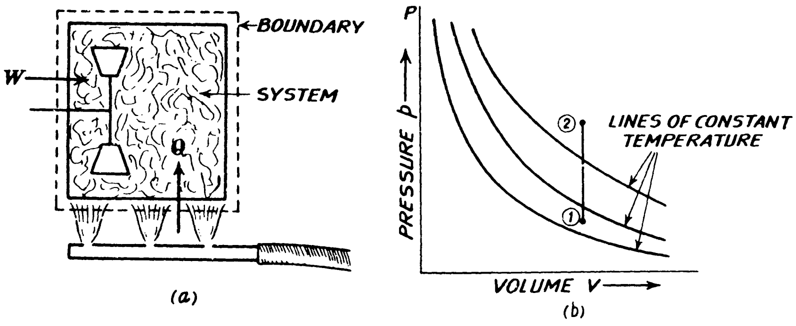


Fig. 1.8

The boundary of the system is rigid. Paddle work may be there. Thus work done by the system is zero, and due to heat addition to the system and paddle-work done on the system, there is increase in internal energy. Thus

$$_1Q_2 = (U_2 - U_1) \qquad \text{...(1.21)}$$

or

$$\delta Q = dU \qquad \text{...(1.22)}$$

i.e. during a constant volume process, the heat transfer equals the change in internal energy of the system. Addition of heat to the system increases internal energy and rejection of heat from the system decreases internal energy.

Thus $\delta Q = dU = mC_v dT$

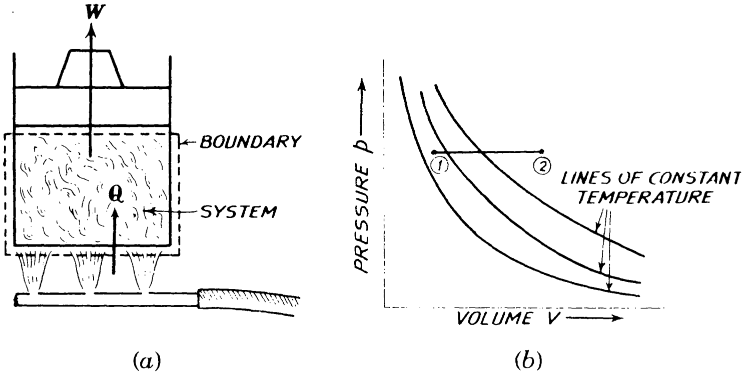
For unit mass,

$$\delta q = du = C_v dT \qquad \text{...(1.23)}$$

or $$\left(\frac{du}{dT}\right)_v = C_v \qquad \text{...(1.24)}$$

i.e. specific heat of fluid at constant volume is the rate of change of of internal energy with respect to absolute temperature.

(*ii*) **Constant pressure process or Isobaric Process.** Refer Fig. 1.9. In a constant pressure process, the system is subjected to constant hydrostatic pressure at the boundaries. It is illustrated by fluid contained in cylinder and piston with weight is placed on the fluid. By the expansion of the fluid due to addition of heat the piston rises and thus changes the system boundary and displacement work is done *by* the system against a constant force. Rejection of heat will lead to contraction and the piston will descend, thus displacement work being done *on* the system. If the process is carried out in thermodynamic equilibrium, *i.e.* it is a quasi-static process, the work done $\delta W = pdV$ and the First Law of Thermodynamics for a process is written as



(*a*) (*b*)

Fig. 1.9

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

Since p is constant through the process

$$\delta Q = dU + d(pV)$$
$$= d(U + pV)$$
$$= dH \qquad \text{...(1.25)}$$

where H is known as the enthalpy.

Thus, during constant pressure process, heat transfer is equal to change in enthalpy.

or $$\delta Q = dH$$
$$= mC_p dT \qquad \text{...(1.26)}$$

For unit mass

$$\delta q = dh = C_p dT \qquad \text{...(1.27)}$$

or
$$\left(\frac{dh}{dT}\right)_p = C_p \qquad \text{...(1.28)}$$

i.e. specific heat at constant pressure is the rate of change of specific enthalpy with respect to absolute temperature.

Enthalpy. Sum of internal energy and pressure volume product, *i.e.* $(U + pV)$ is known as enthalpy. $H = U + pV$, taking proper care about the units on both side of the equation. Since right side of the equation has each of the quantities as properties, enthalpy is also a property. For unit mass, $h = u + pv$.

We have
$$h = u + pv \qquad \text{...(1.29)}$$

Or
$$dh = du + pdv + vdp \qquad \text{...(1.30)}$$

i.e.
$$\begin{aligned} pdv &= dh - vdp - du \\ &= C_p dT - vdp - C_v dT \qquad \text{...(1.32)} \end{aligned}$$

Thus First Law of Thermodynamics can be written as

$$\begin{aligned} \delta q &= du + pdv \qquad \text{...(1.33)} \\ &= C_v dT + pdv \qquad \text{...(1.34)} \\ &= dh - vdp \qquad \text{...(1.35)} \\ &= C_p dT - vdp \qquad \text{...(1.36)} \end{aligned}$$

Also for perfect gas,

$$h = u + pv = u + RT \qquad \text{...(1.36 } a)$$

or
$$dh = du + RdT \qquad \text{...(1.36 } b)$$

or
$$\frac{dh}{dT} = \frac{du}{dT} + R \qquad \text{...(1.36 } c)$$

i.e.
$$C_p = C_v + R \qquad \text{...(1.36 } d)$$

or
$$C_p - C_v = R \qquad \text{...(1.36 } e)$$

(*iii*) **Constant temperature process or Isothermal process** Refer Fig. 1.10. It illustrates that the system boundary is movable and, therefore, displacement work is present but the system temperature is maintained constant by contact of the system with a constant temperature reservoir. Thus it is obvious that during expansion, the volume will increase, but the force on the piston must decrease, and *vice versa* during compression. Therefore, the following relationship for a perfect *gas* holds $pv = RT$ = constant.

Thus pressure volume product is constant for a perfect gas in the case of isothermal process. And according to First Law of Thermodynamics $\delta Q = dU + \delta W = dU + pdV$.

But $dU = 0$ for a gas, since there is no temperature rise.

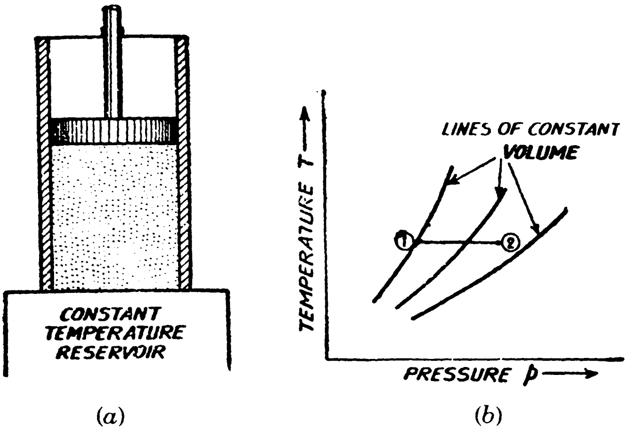


Fig. 1.10

Therefore $\delta Q = pdV$ (for gas)

or $${}_1Q_2 = \int_1^2 pdV \qquad \text{...(1.37)}$$

(*iv*) **Reversible adiabatic process.** If a process occurs in such a way that there is no heat transfer between the surroundings and the system but the boundary of the system moves giving displacement work, the process is said to be adiabatic. Such a process is possible if the system is thermally insulated from the surroundings.

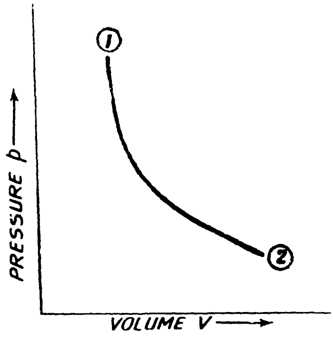


Fig. 1.11

According to First Law of Thermodynamics

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

But $\delta Q = 0$

Therefore, $\delta W = -dU$ ...(1.38)

Thus work is done by the system at the cost of internal energy,

or $$\delta W = -dU = -mC_v dT \qquad \text{...(1.39)}$$

If the expansion and compression process is slow behind a frictionless piston

$$\delta W = pdV$$

or $$pdV = -dU \qquad \text{...(1.40)}$$

or $$pdV + dU = 0 \qquad \text{...(1.41)}$$

Therefore, *for a perfect gas*

$$pdV + mC_v dT = 0 \qquad \text{...(1.42)}$$

and

$$pV = mRT$$

or

$$pdV + Vdp = mRdT \qquad \text{...(1.43)}$$

For unit mass

$$pdv + C_v dT = 0 \qquad \text{...(1.44)}$$

and

$$pdv + vdp = RdT \qquad \text{...(1.45)}$$

Therefore, equations (1.44) and (1.45) are re-written as

$$pdv + C_v dT = 0 \qquad \text{...(1.46)}$$

and

$$pdv + vdp = RdT \qquad \text{...(1.47)}$$

From (1.46) and (1.47), we have

$$C_v\left(\frac{pdv + vdp}{R}\right) + pdv = 0 \qquad \text{...(1.48)}$$

or

$$C_v(pdv + vdp) + R\,pdv = 0 \qquad \text{...(1.49)}$$

i.e.

$$C_v(pdv + vdp) + pdv(C_p - C_v) = 0 \qquad \text{...(1.50)}$$

Therefore, $C_v vdp + C_p pdv = 0$ ...(1.51)

Dividing throughout by $C_p pv$, we get

$$\frac{dp}{p} + \frac{C_p}{C_v}\frac{dv}{v} = 0 \qquad \text{...(1.52)}$$

i.e.

$$\frac{dp}{p} + \gamma\frac{dv}{v} = 0 \qquad \text{...(1.53)}$$

Integrating we get

$$\log_e p + \gamma \log_e v = \text{constant} \qquad \text{...(1.54)}$$

$$= \log_e \text{(another constant)}$$

Therefore, $pv^\gamma = C$ ...(1.55)

Fig. 1.11 illustrates the curve given by equation (1.55) on p-v co-ordinates.

Equations (1.55) may also be written in the following forms for the two end states reached during a process.

(*i*) $p_1v_1^\gamma = p_2v_2^\gamma$ ...(1.56)

(*ii*) $$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1}\right)^{\gamma - 1} \qquad \text{...(1.57)}$$

(*iii*) $$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{\gamma - 1}{\gamma}} \qquad \text{...(1.58)}$$

Equation (1.55) also helps in evaluation of *pdv* work during the process.

Work done during the process per kg of working substances

$$ {}_1w_2 = \int_{v_1}^{v_2} p\,dv $$

But $$ pv^{\gamma} = C $$

or $$ p = \frac{C}{v^{\gamma}} $$

∴ $$ {}_1w_2 = \int_{v_1}^{v_2} \frac{C}{v^{\gamma}}\,dv $$

$$ = C\int_{1}^{v_2} v^{-\gamma}\,dv $$

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

Put $$ C = p_1 v_1^{\gamma} = p_2 v_2^{\gamma} $$

Therefore $$ {}_1w_2 = \frac{p_2 v_2 - p_1 v_1}{-\gamma+1} $$

or $$ {}_1w_2 = \frac{p_1 v_1 - p_2 v_2}{\gamma-1} \qquad \text{...(1.59)} $$

Also, $$ {}_1w_2 = \frac{p_1 v_1 - p_2 v_2}{\gamma-1} \text{ Nm/kg or J/kg} \qquad \text{...(1.60)} $$

if p is expressed in N/m^2

and $$ {}_1w_2 = \frac{R(T_1 - T_2)}{\gamma-1} \text{ Nm/kg or J/kg} \qquad \text{...(1.61)} $$

if R is expressed in Nm/kg °K or J/kg °K

or $$ {}_1w_2 = \frac{R(T_1 - T_2)}{(\gamma-1)} \text{ kJ/kg} \qquad \text{...(1.62)} $$

if R is expressed in kJ/kg °K

(*vi*) **Polytropic reversible process.** Equation (1.55) is very convenient form for engineering calculations. Generalised form of equation for pressure volume relationship can be written as

$$ pv^n = C $$

where n is called the polytropic index of compression or expansion and the following equation can be written by analogy to equations for the reversible adiabatic process which is only a special case of polytropic process with $n = \gamma$.

$$ p_1 v_1^{n} = p_2 v_2^{n} \qquad \text{...(1.63)} $$

$$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1}\right)^{n-1} \qquad \text{...(1.64)}$$

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{n-1}{n}} \qquad \text{...(1.65)}$$

$$_1w_2 = \frac{p_1v_1 - p_2v_2}{n-1} \qquad \text{...(1.66)}$$

Fig. 1.12 shows a number of reversible polytropic process on the p-v plane. Considering the starting point as (1), fourth quadrant will contain expansion processes and second quadrant will contain compression processes. For a perfect gas, if $n = 0$ is substituted in the equation for polytropic process, equation for constant pressure process is obtained. Similarly, $n = \propto$ and $n = 1$ give constant volume and constant temperature processes respectively.

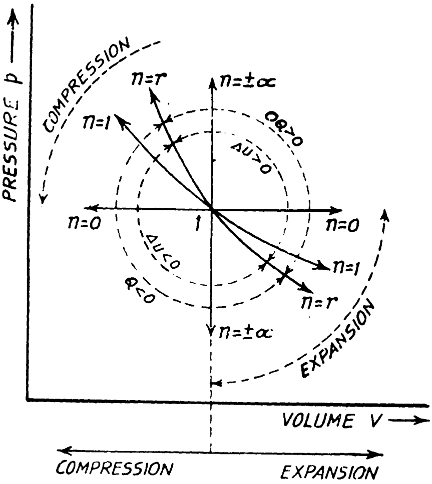


Fig. 1.2

Heat transfer during polytropic process (for perfect gas pv = RT).

Heat transfer per unit mass

$$_1q_2 = (u_2 - u_1) + \int_1^2 p\,dv$$

$$= C_v\,(T_2 - T_1) + \frac{R(T_2 - T_1)}{1-n}$$

$$= \left(C_v + \frac{R}{1-n}\right)(T_2 - T_1) \qquad \text{...(1.67)}$$

Also enthalpy $\quad h = u + pv$

or $\quad dh = d(u + pv)$

i.e. $\quad C_p dT = d(u + pv)$

$$\therefore \quad C_p = \frac{d(u+pv)}{dT} = \frac{d(u+RT)}{dT}$$

$$= \frac{du}{dT} + R$$

Table 2

Summary of processes for perfect gas (unit mass)

Equation must be used keeping dimensional consistence

Process	*Constant pressure*	*Constant volume*	*Constant temperature*	*Reversible adiabatic*	*Polytropic*
Index n	$n = 0$	$n = \propto$	$n = 1$	$n = \gamma$	$n = n$
pvT relations	$\frac{T_2}{T_1} = \frac{v_2}{v_1}$ (Boyle's law)	$\frac{T_2}{T_1} = \frac{p_1}{p_2}$	$p_1v_2 = p_2v_2$ (Charles' law)	$p_1{v_1}^{\gamma} = p_2{v_2}^{\gamma}$ $\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma - 1}$ $= \left(\frac{p_2}{p_1}\right)^{\frac{\gamma - 1}{\gamma}}$	$p_1{v_1}^{n} = p_2{v_2}^{n}$ $\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n - 1}$ $= \left(\frac{p_1}{p_2}\right)^{\frac{n - 1}{n}}$
Heat added	$C_p(T_2 - T_1)$	$C_v(T_2 - T_1)$	$p_1v_2 \log \frac{v_2}{v_1}$	0	$C_n(T_2 - T_1)$ $= C_v\left(\frac{\gamma - n}{1 - n}\right)(T_2 - T_1)$
$\int_0^2 pdv$	$p_1(v_2 - v_1)$	0	$p_1v_1 \log \frac{v_2}{v_1}$	$\frac{p_2v_2 - p_1v_1}{1 - \gamma}$	$\frac{p_2v_2 - p_1v_1}{1 - n}$
Specific heat C	C_p	C_v	$\propto$	0	$C_n = C_v\left(\frac{\gamma - n}{1 - n}\right)$

Thus $C_p = C_v + R$

or $(C_p - C_v) = R$ ...(1.68)

Substituting equation (1.68) in (1.66), we get

$$ {}_1q_2 = \frac{C_p - nC_v}{1 - n}(T_2 - T_1) \quad \text{...(1.69)}$$

$$ = C_n(T_2 - T_1) \quad \text{...(1.70)}$$

where $C_n = \dfrac{C_p - nC_v}{1 - n}$

is called polytropic specific heat.

Substituting $\dfrac{C_p}{C_v} = \gamma_v$, we get

$$C_n = \left(\frac{\gamma - n}{1 - n}\right)C_v \quad \text{...(1.71)}$$

and the equation for heat transfer is modified as

$$ {}_1q_2 = \left(\frac{\gamma - n}{1 - n}\right)C_v(T_2 - T_1) \quad \text{...(1.72)}$$

1.34. Irreversible Process. Except for the free expansion process, we have hitherto considered reversible processes, when the work could be written in the form $w = \int pdv$. But in free expansion which is an irreversible process it was noted that $\int pdv \neq 0$ and work $= w = 0$. Also when paddle work is done on the system without changing the boundaries of the system or keeping the boundaries fixed, $\int pdv = 0$. But work, $w \neq 0$. The paddle work done on the system is more or less equivalent of work dissipated in the system due to turbulence. And the expression $\int pdv$ is used only when the process is quasi-static and there is change in system boundaries.

It is observed, that in actual practice, most of the processes are irreversible, due to turbulence in the system, temperature gradients in the system, and due to friction. These can be taken care of, if the end states in a process are in thermodynamic equilibrium. Thus first law of thermodynamic may be rewritten taking the above situation into account as follows : (For unit mass)

$$q = \Delta u + \int pdv - w_{dissipated} \quad \text{...(1.73)}$$

or

$$ {}_1q_2 = (u_2 - u_1) + \int_0^2 pdv - w_{dissipated} \quad \text{...(1.74)}$$

Table 3. Summary of Properties for Perfect Gas

(The values are fairly accurate for the purpose of the use in the text book)

S. No.	*Gas*	*Chemical formula*	*Number of atoms in 1 molecule*	*Molecular weight*	*Specific weight or kg/m^3 S.T.P.*	*Gas constant R kJ/kg °K*	*Specific heat at constant pressure C_p kcal/kg*	$\gamma = C_p/C_v$
1.	Helium	He	1	4.003	0.179	2.075	5.230	1.68
2.	Air	—	2	29	1.293	0.287	1.005	1.4
3.	Oxygen	O_2	2	32	1.429	0.26	0.200	1.4
4.	Hydrogen	H_2	2	2.016	0.09	4.125	14.25	1.4
5.	Nitrogen	N_2	2	28.016	1.251	0.297	1.042	1.4
6.	Carbon monoxide	CO	2	28	1.25	0.297	1.046	1.4
7.	Carbon dioxide	CO_2	3	44	1.963	0.189	0.846	1.3
8.	Methane	CH_4	5	16.032	0.715	0.52	2.168	1.31
9.	Ethylene	C_2H_4	6	28.032	1.2514	0.297	1.511	1.25

It may be noted that $\gamma = C_p / C_v$ is 1.4 for all diatomic gases and and 1.68 for all monoatomic gases and for polyatomic gases there is a considerable deviation from 1.3.

It may be noted that, in irreversible expansion process the net work output is less than $\int pdv$ and is given by

$$w_{net} = \left[\int pdv - w_{dissipated}\right] \quad ...(1.75)$$

Similarly for irreversible compression proeess, the network input to the system is greater than $\int pdv$ and is given by

$$w_{net} = \left[-\int pdv - w_{dissipated}\right] \quad ...(1.76)$$

1.35. Flow Process and Control Volume. In most engineering plants, the substance continuously flows in and out of the component. Fig. 1.13 shows diagrammatically a heating chamber or a boiler, where heat Q is added in a turbine where shaft work W_s is taken out, while the fluid is continuously flowing in and out. In such cases, the non-flow analysis to compute work and heat transfer across the system is not feasible. In the analysis of such process, called flow process, a concept of control volume is introduced. Imaginary boundaries are put around the component to be studied as shown in Fig. 1.13. The space bounded by these boundaries is called the control volume. It is a volume of fixed shape and position. The difference between system and control volume is that the boundary of the system may change, but the control volume boundary is fixed, the matter flows across the boundary of the control volume.

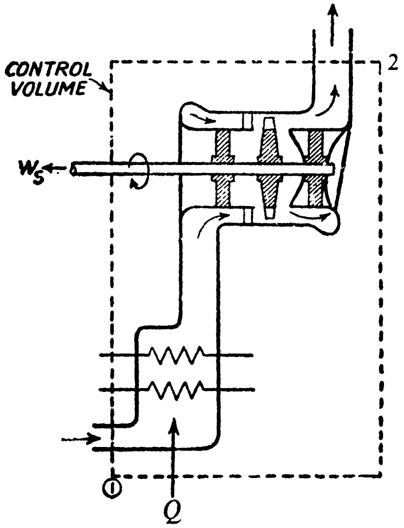


Fig. 1.13

1.36. Steady Flow Energy Equation. Mostly in engineering applications, the situations occur when the steady flow conditions are assumed. The conditions to be satisfied are the following :

(*i*) the mass flow rate through the control volume is constant ;

(*ii*) the state of substance passing through the control volume at all the locations remains constant ;

(*iii*) the transfer of heat and work from or to the control volume is constant. Thus for unit mass flow,

$$\left(u_1 + p_1 v_1 + \frac{\mathrm{v}_1^2}{2} + g\,z_1\right) + q = \left(u_2 + p_2 v_2 + \frac{\mathrm{v}_2^2}{2} + g\,z_2\right) + w_s \qquad \text{...(1.78)}$$

For mass m equation (1.78) reduces to

$$m\left(u_1 + p_1 v_1 + \frac{\mathrm{v}_1^2}{2} + g\,z_1\right) + Q = m\left(u_2 + p_2 v_2 + \frac{\mathrm{v}_2^2}{2} + g\,z_2\right) + W_s \qquad \text{...(1.78)}$$

Equation (1.78) is called steady flow energy equation.

Substituting $h = u + pv$, it reduces to

$$m\left(h_1 + \frac{\mathrm{v}_1^2}{2} + g\,z_1\right) + {}_1Q_2 = m\left(h_2 + \frac{\mathrm{v}_2^2}{2} + g\,z_2\right) + W_s \qquad \text{...(1.79 a)}$$

N.B. All the quantities in equations must be expressed in consistent units. For example :

If Q = heat transfer across the control volume in J

W_s = shaft work crossing the control volume in N-m

h = enthalpy in J/kg

v = velocity in m/sec

z = elevation in m

m = mass in kg

$$m\left(h_1 + \frac{\mathrm{v}_1^2}{2} + g\,z_1\right) {}_1Q_2 = m\left(h_2 + \frac{\mathrm{v}_2^2}{2} + g\,z_2\right) + W_s \qquad \text{...(1.79 b)}$$

1.37. Flow Processes. The steady flow energy equation for unit mass flow is given by, (dimensional consistence to be checked when nsed).

$$h_1 + \frac{\mathrm{v}_1^2}{2} + g\,z_1 + q = h_2 + \frac{\mathrm{v}_2^2}{2} + g\,z_2 + W_s \qquad \text{...(1.80)}$$

It can also be written in the form

$$dh + d\left(\frac{\mathrm{v}^2}{2}\right) + d\,(g\,z) = \delta q - \delta w_s \qquad \text{...(1.81)}$$

Also $h = u + pv$

Therefore, $$dh = du + pdv + vdp \qquad \text{...(1.82)}$$

Thus $$du + pdv + vdp + d\left(\frac{\mathrm{v}^2}{2}\right) + d(g\,z) = \delta q - \delta w_s \qquad \text{...(1.83)}$$

According to the First Law of Thermodynamics, for the moving system, to an observer moving with the fluid, the attention gets focused on a seemingly stationary system, and therefore,

$$du + pdv = \delta q \qquad \text{...(1.84)}$$

i.e. equation (1.84) holds good for flow as well as non-flow processes.

Therefore, equation get reduced to,

$$vdp + d\left(\frac{\mathrm{v}^2}{2}\right) + d(g\,z) = -\,\delta w_s \qquad \text{...(1.85)}$$

i.e. $$\delta w_s = -\,vdp - d\left(\frac{\mathrm{v}^2}{2}\right) - d(g\,z) \qquad \text{...(1.86)}$$

Therefore $$w_s = -\int_{p_1}^{p_2} vdp - \frac{\mathrm{v}_2^{\,2} - \mathrm{v}_1^{\,2}}{2} - (z_2 - z_1)g \qquad \text{...(1.87)}$$

If the kinetic energy and potential energy changes are negligible, equation (1.87) reduces to

$$w_s = -\int_{p_1}^{p_2} vdp \qquad \text{...(1.88)}$$

Result of equation (1.88) may be derived by reference to Fig. 1.14 (*a*) and (*b*) drawn for unit mass flow.

$$\text{Area } a\text{-}1\text{-}2\text{-}b = -\int_{p_1}^{p_2} vdp \qquad \text{...(1.89)}$$

$$\text{Area } e\text{-}1\text{-}2\text{-}f = \int_{v_1}^{v_2} pdv \qquad \text{...(1.90)}$$

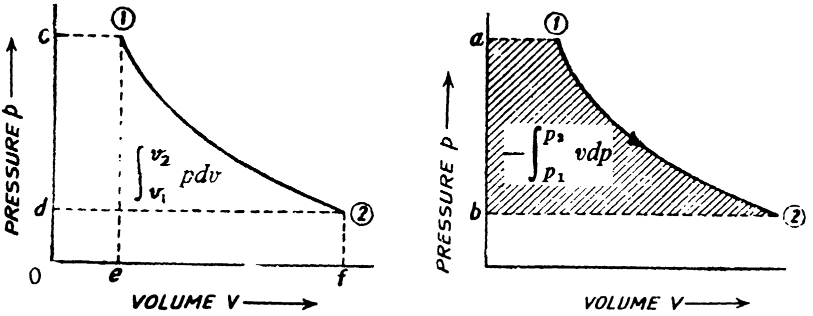


Fig. 1.14

Area *a*-1-2-*b* is same as area *c*-1-2-*d*.

But area *c*-1-2-*d* = area *c*-1-*e*-0 + area *e*-1-2-*f* – area *d*-2-*f*-0

$$= p_1v_1 + \int_{v_1}^{v_2} pdv - p_2v_2$$

There $p_1v_1 + \int_{v_1}^{v_2} pdv - p_2v_2 = -\int_{p_1}^{p_2} vdp$ ...(1.91)

In equation (1.91),

p_1v_1 = flow work coming to the control volume by unit mass of fluid coming in the control volume.

p_2v_2 = flow work going out of the control volume by unit mass of fluid going out of the control volume.

$\int_{v_1}^{v_2} pdv$ = work done within the control volume, or the net work ...(1.92)

$-\int_{p_1}^{p_2} vdp$ = the shaft work ...(1.93)

$(p_2v_2 - p_1v_1)$ = flow work change. ...(1.93 *a*)

The steady flow energy equation may also be written in the differential form as

$$du + d(pv) + d\left(\frac{\mathrm{v}^2}{2}\right) + d\,(gz) = \delta q - \delta w_s \qquad ...(1.94)$$

i.e. $\delta q = du + dw_f + dK + dP + \delta w_s$ ...(1.95)

where dw_f = change in flow work/unit mass

dP = change in potential energy/unit mass

dK = change in kinetic energy/unit mass

δw_s = shaft work/unit mass.

1.38. Heat Engine. A heat engine is a cyclically operating system across whose boundary flow only heat and work. This definition includes any device operating cyclically and its primary purpose being transformation heat of into work. Thus, if we consider boiler, turbine, condenser and pump separately in a power plant, they do not get included in the definition of heat engines, as in each of the devices, the system does not complete a cycle. But all these devices when put together satisfy the definition of heat engine. Referring to Fig. 1.15, we note that heat enters the system at the boiler and

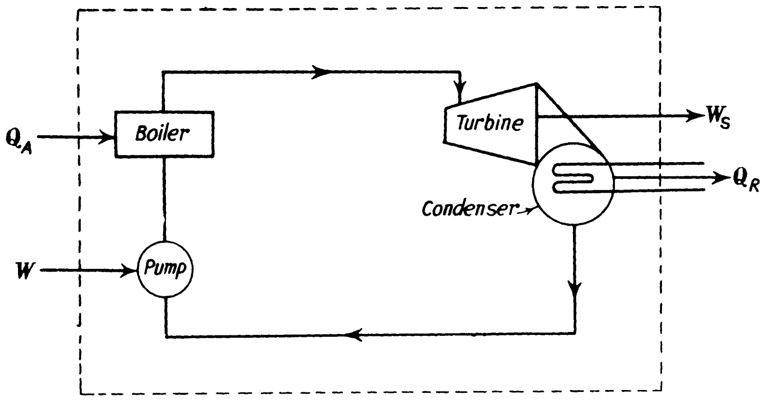


Fig. 1.15

leaves at the condenser. The difference between these equals work at the turbine and pump, *i.e.*

$$(Q_A - Q_R) = (W_S - W) \qquad \text{...(1.96)}$$

The working fluid is water, and it undergoes a cycle of processes, passing from boiler and having changed to steam there, goes to turbine and then to condenser where it change back to water and goes to pump and then finally to the boiler. Thus cycle is completed. Thus the working fluid has eventually been returned to its initial state.

1.39. Thermal Efficiency of Heat Engine. The efficiency of any device is the ratio of output energy sought to the input energy. In the heat engine referred to in Art. 1.38, the output energy sought is the network done by the system on the surroundings, since the purpose of this heat engine is to convert heat into work. Thus thermal efficiency denoted by η_{th} is given by

$$\text{Efficiency} = \frac{\text{Energy effect sought}}{\text{Energy input required}}$$

$$\eta_{th} = \frac{W_{turbine} - W_{pump}}{Q_A}$$

$$= \frac{Q_A - Q_R}{Q_A} \qquad \text{...(1.97)}$$

The quantity Q_R is enormous, and it is often 60 to 70% of Q_A in actual practice. Thus thermal efficiency may be as high as only 30 to 40%, in actual practice.

1.40. Reversible Cycle Carnot Cycle. Sadi Carnot proposed a reversible cycle in which the working medium receives heat at one temperature and rejects heat at another temperature. This will mean that the cycle will consist of two isothermal processes and two reversible adiabatic processes. The proposed reversible engine works as follows. Refer Fig. 1.16. A cylinder has a piston working in it without friction. The walls of the cylinder and the piston are assumed as perfect insulators of heat. The cylinder head is so arranged that it can be a perfect heat conductor as well as a perfect heat insulator. There is a heat source (source is a large reservoir such that transfer of heat from it does not affect its temperature) at temperature T_1 and a heat sink (sink is large reservoir essentially such that transfer of heat to it does not change its temperature) at temperature T_2. The heat source at temperature T_1 is put in contact with gas in the cylinder and the gas expands isothermally at temperature T_1 from the state point (1) to the state point (2) as shown in Fig. 1.17 representing the *p-v* diagram of the process. The external work is done by the system represented by $\int_{v_1}^{v_2} p\,dv$ for unit mass and the law of

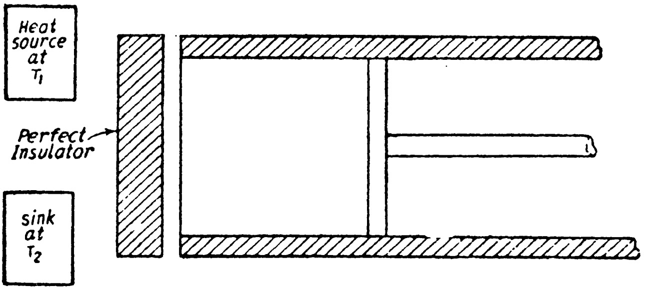


Fig. 1.16

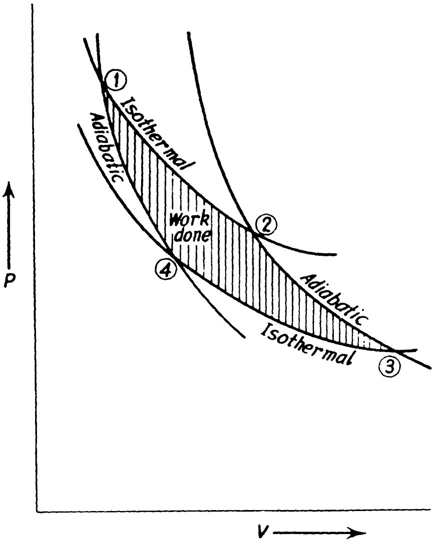


Fig. 1.17

expansion is $pv = C$ with corresponding heat absorbed by the system given by q_A at temperature T_1. The cylinder head which was a perfect conductor is now insulated perfectly. The gas in the cylinder is now allowed to expand further to state point (3), following a reversible adiabatic process. The temperature falls to T_2, the temperature of the sink and no heat is exchanged between the system and surroundings but external work is done represented by $\int_{v_2}^{v_3} p\,dv$ and the law of expansion $pv^\gamma = C$. Now the system is brought into contact with the sink at temperature T_2 and the insulation is removed from a cylinder head to again to make it a perfect conductor. The gas is now compressed isothermally from state point (3) to state point (4). During this process, work is done on the system given by $\int_{v_3}^{v_4} p\,dv$ and a corresponding heat q_R is rejected from the system at temperature T_2. Again, the head is perfectly insulated and the gas compressed to follow the reversible adiabatic law, to state point (1). No heat is interchanged. Thus the cycle is completed. Since the system has completed a cycle and is returned to its initial state, according to First Law of Thermodynamics, its internal energy has not changed.

or $$\text{Cyclic} \int \delta q = \text{cyclic} \int p\,dv$$

or $$q_A - q_R = \text{Work done} = w.$$

And thermal efficiency is given by

$$\eta_{th} = \frac{\text{Work done by the system, } i.e. \text{ energy sought}}{\text{Heat supplied to the system from high temp. source}}$$

$$= \frac{w}{q_A} = \frac{q_A - q_R}{q_A} \qquad \ldots(1.98)$$

Carnot cycle is represented as a standard of perfection and other engines can be compared with it to judge the degree of perfection. It gives the concept of maximising work output between two temperature limits.

Problem 1.5 *Refer to Fig. 1.17. By using perfect gas show that for Carnot cycle the efficiency is a function of temperature only and that* $\int \frac{\delta q}{T} = 0$ *when the integration is carried over the whole cycle or cyclic integral of* $\frac{\delta q}{T} = 0$. *Justify the statement that efficiency depends* *only on temperature difference and is independent of the working substances.*

Solution. Let p_1, v_1 T_1 ; p_2, v_2 T_2 ; p_3, v_3, T_3 and p_4 v_4, T_4 denote the four points 1, 2, 3 and 4 on the p-v diagram.

Process 1-2. $pv = C$; $\Delta u = 0$

$$_1q_2 = {_1w_2} = \int_1^2 pdv = RT_1 \log_e \frac{p_1}{p_2}$$

Process 2-3. $pv^\gamma = C$; $_2q_3 = 0$

$$_2w_3 = (u_2 - u_3) = + C_v(T_2 - T_3).$$

Process 3-4. $pv = C$; $\Delta u = 0$

$$_3q_4 = w = -RT_3 \log_e \frac{p_4}{p_3}.$$

Process 4-1. $pv^\gamma = C$; $_4q_3 = 0$

$$_4w_1 = -(u_1 - u_4) = -C_v(T_1 - T_4)$$

Net work done per kg of working substance

$$\text{Cyclic} \int \delta w = \text{cyclic} \int \delta q = RT_1 \log_e \frac{p_1}{p_2} - RT_3 \log_e \frac{p_4}{p_3}.$$

Since 2-3 and 4-1 are reversible adiabatics

$$\frac{p_2}{p_3} = \left(\frac{T_2}{T_3}\right)^{\frac{\gamma}{\gamma-1}}$$

$$\frac{p_1}{p_4} = \left(\frac{T_1}{T_4}\right)^{\frac{\gamma}{\gamma-1}}$$

But $T_2 = T_1$ and $T_3 = T_4$

$$\therefore \quad \frac{p_2}{p_3} = \frac{p_1}{p_4} \quad \text{or} \quad \frac{p_1}{p_2} = \frac{p_4}{p_3}.$$

Therefore, network done per kg of working substance

$$= RT_1 \log \frac{p_1}{p_2} - RT_3 \log_e \frac{p_4}{p_3}$$

$$= R(T_1 - T_3) \log_e \frac{p_1}{p_2}$$

and heat input $_1q_2 = RT_1 \log_e \frac{p_1}{p_2}$

$$\therefore \quad \eta_{th} = \frac{R(T_1 - T_3) \log_e p_1/p_2}{RT_1 \log_e p_1/p_2} \qquad \text{...(1.99)}$$

$$= \frac{T_1 - T_3}{T_1} \qquad ...(1.100)$$

Thus, it is proved that Carnot efficiency depends only on temperature difference of source and sink and is independent of the working substance.

Now for Process 1-2 $\int \frac{\delta q}{T} = R \log_e \frac{p_1}{p_2}$

Now for Process 2-3 $\int \frac{\delta q}{T} = 0$

Now for Process 3-4 $\int \frac{\delta q}{T} = -R \log_e \frac{p_4}{p_3} = -R \log_e \frac{p_1}{p_2}$

Now for Process 4-1 $\int \frac{\delta q}{T} = 0$

Therefore, cyclic $\int \frac{\delta q}{T} = 0$ ...(1.101)

1.41. Entropy. For a reversible cycle,

$$\text{Cyclic} \int \left(\frac{\delta Q}{T} \right)_{rev} = 0$$

or

$$\left(\frac{\delta Q}{T} \right)_{rev} = dS \qquad ...(1.102)$$

where S is called entropy,
or change in entropy during a reversible process can be written as

$$\int_1^2 \left(\frac{\delta Q}{T} \right)_{rev} = \int_1^2 dS = (S_2 - S_1) = \Delta S \qquad ...(1.103)$$

For unit mass

$$\int_1^2 \left(\frac{\delta q}{T} \right)_{rev} = \int_1^2 ds = \Delta s \qquad ...(1.104)$$

1.42. Entropy changes during processes

We have

$$\Delta S = \int \left(\frac{\delta Q}{T} \right)_{rev}$$

or

$$\Delta S = \int \left(\frac{dU + \delta W}{T} \right)_{rev} \qquad ...(1.105)$$

or
$$\Delta S = \int \left(\frac{dU + pdV}{T} \right) \qquad \text{...(1.106)}$$

The units must be taken care of in the above equations. In the differential form, it can be written as

$$dS = \frac{dU + pdV}{T} \qquad \text{...(1.107)}$$

or
$$TdS = dU + pdV \qquad \text{...(1.108)}$$

This equation is very important since it establishes a relationship between all the thermodynamic properties and does not involve path functions like work and heat. It is interesting, therefore, to note that equations $\delta Q = dU + pdV$, and $\delta Q = TdS$ are true for reversible processes but equation $TdS = dU + pdV$ is true for all processes reversible as well as irreversible. This equation is true for any two equilibrium states of a system.

Also
$$\begin{aligned} TdS &= dU + pdV \\ &= d(H - pV) + pdV \\ &= dH - pdV - Vdp + pdV \\ &= dH - Vdp \end{aligned}$$

Thus
$$TdS = dH - Vdp \qquad \text{...(1.109)}$$

Alternatively

$$(S_2 - S_1) = \int_1^2 \frac{dU}{T} + \int_1^2 \frac{p}{T} dV \qquad \text{...(1.110)}$$

and
$$S_2 - S_1 = \int_1^2 \frac{dH}{T} - \int_1^2 \frac{V}{T} dp \qquad \text{...(1.111)}$$

(*i*) **Constant volume process.** We have for unit mass

$$s_2 - s_1 = \int_1^2 \frac{du}{T} + \int_1^2 \frac{p}{T} dv$$

But
$$dv = 0$$

Therefore,
$$(s_2 - s_2) = \int_1^2 \frac{du}{T}$$

$$= \int_1^2 C_v \frac{dT}{T} \qquad \text{...(1.112)}$$

If C_v is constant for the gas

$$(s_2 - s_2) = C_v \log_e \frac{T_2}{T_1} \qquad \text{...(1.113)}$$

(*ii*) **Constant pressure process.** We have for unit mass

$$(s_2 - s_1) = \int_1^2 \frac{dh}{T} - \int_1^2 \frac{v}{T}\,dp$$

But $dp = 0$

Therefore, $(s_2 - s_1) = \int_1^2 \frac{dh}{T}$

$$= \int_1^2 C_p \frac{dT}{T} \qquad \text{...(1.114)}$$

If C_p is a constant for the gas

$$(s_2 - s_1) = C_p \log_e \frac{T_2}{T_1} \qquad \text{...(1.115)}$$

(*iii*) **Isothermal process.** $pv = C$ $(pv = RT)$

$$(s_2 - s_1) = \int_1^2 \frac{C_v dT}{T} + \int_1^2 \frac{p}{T}\,dv$$

But $dT = 0$

Therefore, $(s_1 - s_2) = \int_1^2 \frac{p}{T}\,dv = \int_1^2 \frac{C}{T}\frac{dv}{v}$

$$= \frac{C}{T} \log_e \frac{v_2}{v_1} \qquad \text{...(1.116)}$$

for a gas $pv = RT$

Therefore, $(s_2 - s_1) = \frac{RT}{T} \log_e \frac{v_2}{v_1}$

$$= R \log_e \frac{v_2}{v_1} \qquad \text{...(1.117)}$$

Alternatively

$$(s_2 - s_1) = \int_1^2 C_p \frac{dT}{T} - \int_1^2 \frac{v}{T}\,dp$$

But $dT = 0$ and $pv = RT$ for a gas

Therefore, $(s_2 - s_1) = -\int_1^2 \frac{RT}{T}\frac{dp}{p}$

$$= -R \log_e \frac{p_2}{p_1} \qquad \text{...(1.118)}$$

(*iv*) **Reversible adiabatic process.** We have for unit mass

$$\Delta s = \int \left(\frac{\delta q}{T} \right)_{rev} \qquad \text{...(1.119)}$$

But $dq = 0$ for adiabatic process

Therefore, $\Delta s = 0$ or the process is isentropic ...(1.120)

Alternatively, for a reversible process, we have for unit mass,

$$\delta w = pdv \text{ and } \delta q = Tds$$

But if the process is adiabatic

$$\delta q = 0$$

or

$$\delta q = 0 = Tds \qquad \text{...(1.121)}$$

But T cannot be zero, therefore, ds must be equal to zero, *Therefore, reversible adiabatic process in an isentropic process.*

(*v*) **Polytropic process PV^n = C.** We have for unit mass

$$(s_2 - s_1) = \int_1^2 \left(\frac{\delta q}{T} \right)_{rev}$$

But (for gas)

$$\delta q = \frac{\gamma - n}{\gamma - 1} pdv \qquad \text{...(1.22)}$$

$$\therefore \quad (s_2 - s_1) = \int_1^2 \frac{\gamma - n}{\gamma - 1} \frac{p}{T} dv \qquad \text{...(1.123)}$$

$$= \int_1^2 = \frac{\gamma - n}{\gamma - 1} \frac{R}{v} dv \text{ for a gas} \qquad \text{...(1.124)}$$

$$= \frac{(\gamma - n)R}{\gamma - 1} \log_e \frac{v_2}{v_1} \qquad \text{...(1.125)}$$

If T is expressed in °K
u is expressed in J/kg
h is expressed in J/kg
p is expressed in N/m^2
v is expressed in m^3/kg
R is expressed in J/kg °K
s is expressed in J/kg °K
C_v, C_p and C_n are expressed in J/kg °K.

The equations for entropy change may be modified as

$$Tds = du + pdv \qquad \text{...(1.126)}$$

$$Tds = dh - vdp \qquad \text{...(1.127)}$$

$$(s_2 - s_1) = C_v \log_e \frac{T_2}{T_1} \text{ for constant volume process}$$

...(1.128)

$$(s_2 - s_1) = C_p \log_e \frac{T_2}{T_1} \text{ for constant pressure process} \qquad \text{...(1.129)}$$

$$(s_2 - s_1) = R \log_e \frac{v_2}{v_1} \text{ for isothermal process}$$

$$= -R \log_e \frac{p_2}{p_1} \text{ for isothermal process} \qquad \text{...(1.130)}$$

$$(s_2 - s_1) = \frac{\gamma - n}{\gamma - 1} R \log_e \frac{v_2}{v_1} \text{ for polytropic process} \qquad \text{...(1.131)}$$

also

$$(s_2 - s_1) = C_n \log_e \frac{T_2}{T_1} \qquad \text{...(1.132)}$$

$$= C_v \left(\frac{\gamma - n}{1 - n} \right) \log_e \frac{T_2}{T_1} \text{ for polytropic process} \qquad \text{...(1.133)}$$

If u is expressed in kJ/kg
h is expressed in kJ/kg
p is expressed in kN/m^2
(kN = kilo Newton. 1 bar = 10^2 kN/m^2)
v is expressed in m^3/kg
R is expressed in kJ/kg °K
C_p, C_v and C_n are expressed in kJ/kg °K.

The equations can be written, as

$$Tds = du + pdv \qquad \text{...(1.134)}$$

$$Tds = dh - vdp \qquad \text{...(1.135)}$$

$$(s_1 - s_2) = C_v \log_e \frac{T_2}{T_1} \text{ for constant volume process} \qquad \text{...(1.136)}$$

$$(s_2 - s_1) = C_p \log_e \frac{T_2}{T_1} \text{ for constant pressure process} \qquad \text{...(1.137)}$$

$$(s_2 - s_1) = R \log_e \frac{v_2}{v_1} \text{ for isothermal process} \qquad \text{...(1.138)}$$

$$(s_2 - s_1) = -R \log_e \frac{p_2}{p_1} \text{ for isothermal process} \qquad \text{...(1.139)}$$

$$(s_2 - s_1) = \frac{\gamma - n}{\gamma - 1} R \log_e \frac{v_2}{v_1} \text{ for polytropic process} \quad ...(1.140)$$

$$(s_2 - s_1) = C_n \log_e \frac{T_2}{T_1} \text{ for polytropic process} \quad ...(1.141)$$

$$(s_2 - s_1) = C_v \left(\frac{\gamma - n}{1 - n} \right) \log_e \frac{T_2}{T_1} \text{ for polytropic process} \quad ...(1.142)$$

1.43. Temperature-Entropy Diagram. We have

$$_1Q_2 = \int_{s_1}^{s_2} TdS \quad ...(1.143)$$

This integral can be represented graphically as the area under the curve drawn on temperature-entropy co-ordinates in the way as $_1W_2 = \int_{V_1}^{V_2} pdV$ is represented on pressure-volume co-ordinates, as shown in Figs. 1.18 and 1.19.

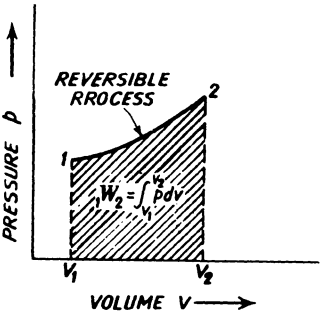


Fig. 1.18

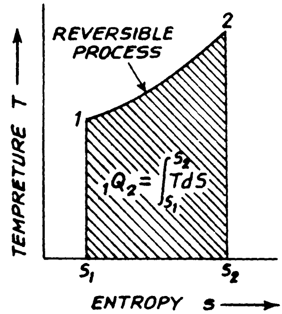
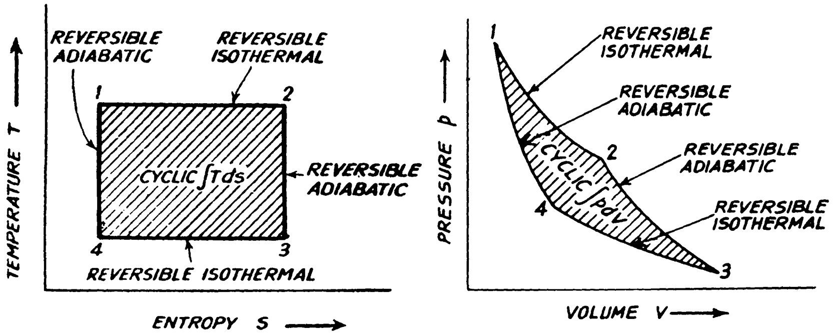


Fig. 1.19

It may be noted that area under the curve representing pdV work on p-V co-ordinates and heat transfer on T-S co-ordinates is valid only for reversible processes. Thus if the same explanation is extended to a cycle of processes, the area enclosed in the cycle of processes on p-V co-ordinates will represent work done in a cycle, and the area enclosed in the cycle of processes on T-S co-ordiantes represents heat transfer, provided of course that all the processes of the cycle are reversible. And by First Law of Thermodyamics

$$\text{cyclic} \int \delta Q = \text{cyclic} \int \delta W.$$

or Heat transferred to the system during cycle
= Work done by the system during cycle.



(a) (b)

Fig. 1.20

This leads to a very important conclusion that the enclosed area for a cycle of processes (reversible) represents work done on both p-V as well as T-S co-ordiantes. Thus, if Cornot cycle is represented on P-V and T-S co-ordinates as shown in Fig. 1.120 (*a*) and (*b*), the hatched area represents work done.

Problem 1.7. *Two bodies, each of equal mass m and heat capacity c are at temperature* T_1 *and* T_2 *respectively.* $(T_1 > T_2)$. *If the first body is used as source of heat for reversible engine and the second as the sink, show that the maximum work obtainable from such arrangement is* $mc\,(\sqrt{T_1} + \sqrt{T_2})^2$.

Solution. Let $T_1 > T_2$ and let the common temperature of two bodies be T_c. Maximum work is obtained when the engine operates along a reversible cycle. In that case, entropy change of the composite system formed by the two bodies is zero. Thus,

$$mc \log_e \frac{T_c}{T_1} + mc \log_e \frac{T_c}{T_2} = 0$$

i.e.
$$mc\left(\log_e \frac{T_c}{T_1} + \log_e \frac{T_c}{T_2}\right) = 0$$

or
$$mc \log_e \frac{T_c^{\,2}}{T_1 T_2} = 0$$

Therefore,
$$\frac{T_c^{\,2}}{T_1 T_2} = 0 \quad \text{or} \quad T_c = \sqrt{T_1 T_2}$$

The work done is given by

$$
\begin{aligned}
W &= \text{heat received} - \text{Heat rejected}\\
&= mc\,(T_1 - T_c) - mc\,(T_c - T_2)\\
&= mc\,[(T_1 - \sqrt{T_1T_2}) - (\sqrt{T_1T_2} - T_2)]\\
&= mc\,[T_1 + T_2 - 2\sqrt{T_1T_2}]\\
&= \mathbf{mc\,[\sqrt{T_1} - \sqrt{T_2}]^2}.
\end{aligned}
$$

Problem 1.8. *An invertor claims that his heat engine has the following specifications. Comment.*

Power developed	*... 76 kW*
Fuel burned per hour	*... 4 kg*
Heating value of the fuel	*... 75,000 kJ / kg.*
Temperature limits	*... 727° and 27°C.*

Solution. We have already proved that the thermal efficiency of Carnot cycle is the maximum between the specified temperature limits.

The Carnot efficiency for the given heat engine

$$
\begin{aligned}
\eta_{Carnot} &= \frac{T_1 - T_2}{T_1}\\
&= \frac{(727 + 273) - (273 + 27)}{(727 + 273)}\\
&= \frac{1000 - 300}{100} = 0.7 \text{ or } 70\%.
\end{aligned}
$$

The actual thermal efficiency claimed

$$
\eta_{Actual} = \frac{\text{Work done}}{\text{Heat supplied}} = \frac{76 \times 1000 \times 60 \times 60}{4 \times 75{,}000 \times 1{,}000}
$$

$$
= \mathbf{0.912 \text{ or } 91.2\% = Not\ possible.}
$$

Problem 1.9. *A carnot heat engine draws heat from a reservoir at temperature T_A and reject heat to another reservoir at temperature T_B. The carnot forward cycle engine drives a carnot reversed cycle engine or carnot refrigerator which absorbs heat from reservoir at temperature T_C and rejects heat to reservoir at temperature T_B. Derive an expression for the ratio of heat absorbed from reservoir at temperature T_C to heat drawn from reservoir at temperature T_A. If the high temperature $T_A = 500°$ and the low temperature $T_C = 250°$ K, determine the temperature T_B such that heat supplied to engine Q_A is equal to heat absorbed by refrigerator Q_C.*

Determine the $\eta_{carnot\ engine}$ and $COP_{Carnot\ refrigerator}$

Solution. Refer Fig. 1.21 for schematic diagram.

$$\eta_{carnot\ engine} = \frac{Q_A - Q_B}{Q_A} = \frac{T_A - T_B}{T_A}$$

$$= \frac{\text{Work of carnot engine}}{\text{Heat supplied to the carnot engine}}$$

$$= \frac{W_{carnot}}{Q_A}$$

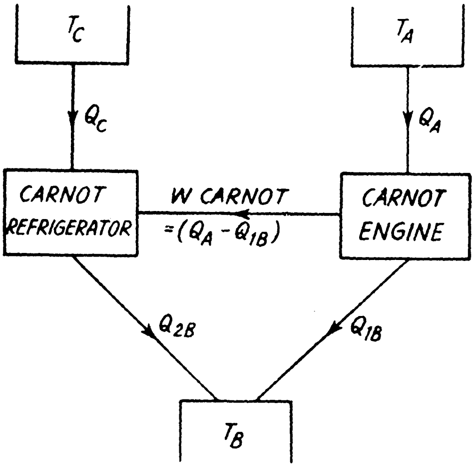


Fig. 1.21

or $$W_{carnot} = Q_A\left[\frac{T_A - T_B}{T_A}\right] \qquad ...(i)$$

Also $COP_{carnot\ refrigerater}$

$$= \frac{Q_C}{Q_{2B} - Q_C} = \frac{T_C}{T_B - T_C}$$

$$= \frac{\text{Heat absorbed}}{W_{carnot}} = \frac{Q_C}{W_{carnot}}$$

or $$W_{carnot} = Q_C\left[\frac{T_B - T_C}{T_C}\right]$$

Therefore $$\frac{Q_C}{Q_A} = \left[\frac{T_A - T_B}{T_A}\right] \Big/ \left[\frac{T_B - T_C}{T_C}\right]$$

or $$\frac{Q_C}{Q_A} = \frac{T_C}{T_A}\left[\frac{T_A - T_B}{T_B - T_C}\right]$$

Thus $$\frac{Q_C}{Q_A} = 1 = \frac{250}{500}\left[\frac{500 - T_B}{T_B - 250}\right]$$

or $$500 - T_B = 2(T_B - 250)$$

or $$3T_B = 1000$$

Thus $$T_B = \frac{1000}{3} = \mathbf{333.33°K.}$$

$$\eta_{carnot\ engine} = \frac{T_A - T_B}{T_A} = \frac{500 - 333.3}{500} = \frac{166.67}{500}$$

$$= \mathbf{0.334} \text{ or } \mathbf{33.4\%}$$

$$\eta_{carnot\ refrigerator} = \frac{T_C}{T_B - T_C}$$

$$= \frac{250}{333.33 - 250}$$

$$= \frac{250}{83.33} = 3.$$

$\eta_{carnot\ refrigerator}$ is normally expressed as COP of the carnot refrigerator.