1

Review of Thermo-Dynamics

1.1. Introduction to S.I. Units

(A) S.I. Units : Fundamental Units or S.I. Base Units. Quantity, unit, symbol and definition of the base units are given below :

(*i*) **Length : metre (m).** The metre is the length of the path travelled by light in vacuum during a time interval of $\frac{1}{299792458}$ of a second.

(*ii*) **Mass : kilogram (kg).** The kilogram is the unit of mass ; it is equal to the mass of the international prototype of the kilogram.

This international prototype is made of platinum-irridium and is kept at the International Bureau of Weights and Measures, Sevres, Paris, France.

(*iii*) **Time : second (s).** The second is the duration of 9192631770 periods of the radiation corresponding to the transition between the two hypertine levels of the ground state of the caesium-133 atom.

(*iv*) **Electric current : Ampere (A).** The ampere is that constant current which, if maintained in two straight parallel conductors and placed 1 metre apart in vacuum, would produce between these conductors a forced equal to 2×10^{-7} newton per metre of length.

(*v*) **Thermodynamic Temperature : Kelvin (K).** The Kelvin, unit of thermodynamic temperature is the fraction $\frac{1}{273.16}$ of the thermodynamic temperature of the triple point of water.

(*vi*) **Luminous intensity : candela (cd).** The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation frequency 540×10^{12} hertz and that has a radiant intensity in that direction as $\frac{1}{683}$ watts per steradian.

(*vii*) **Amount of substance : mole (mol).** The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12.

(B) **S.I. supplementary units :**

(*i*) **Plane angle : radian (rad).** The radian is the plane angle between two radii of a circle which cut off the circumference of an arc equal in length to the radius.

(*ii*) **Solid angle : steradian (sr).** The steradian is the solid angle which, having its vertex in the centre of the sphere, cuts off an area of the surface of sphere equal to that of a square with sides of length equal to the radius of the sphere.

(C) Examples of S.I. derived units expressed in terms of base units :

Quantity	*S.I. units name*	*Symbol*
area	square metre	m^2
volume	cubic metre	m^3
speed, velocity	metre per second	m/s
acceleration	metre per second squared	m/s^2
density, mass density	kilogram per cubic metre	kg/m^3
specific volume	cubic metre per kilogram	m^3/kg

(D) Examples of S.I. derived units with special names :

Quantity	*S.I. unit name*	*Symbol*	*Expression in terms of other unit*	*Expression in terms of S.I. base units*
Force	Newton	N	—	$m\ kg\ s^{-2}$
Pressure, stress	Pascal	Pa	N/m^2	$m^{-1}\ kg\ s^{-2}$
Energy, work Quantity of heat	Joule	J	N-m	$m^2\ kg\ s^{-2}$
Celsius Temperature	degree	°C	—	K

(E) Examples of S.I., derived units expressed by special names :

Quantity	*S.I. unit name*	*Symbol*	*Expression in terms of S.I. base units*
dynamic viscosity	pascal second	Pas	$m^{-1}\ kg\ s^{-1}$
moment of force	metre newton	N-m	$m^2\ kg\ s^{-2}$
surface tension	Newton per metre	N/m	$kg\ s^{-2}$
heat capacity, entropy	Joule per Kelvin	J/K	$m^2\ kg\ s^{-2}\ K^{-1}$
Specific heat capacity, specific entropy	Joule per kilogram kelvin	J/(kg K)	$m^2\ s^{-2}\ K^{-1}$
Specific energy	Joule per kilogram	J/kg	$m^2\ s^{-2}$
Thermal conductivity	Watt per metre Kelvin	W (m K)	$m\ kg\ s^{-3}\ K^{-1}$

(F) S.I. prefixes :

Factor	*Prefix*	*Symbol*	*Factor*	*Prefix*	*Symbol*
10^{18}	exa	E	10^{-1}	deci	*d*
10^{15}	peta	P	10^{-2}	centi	*c*
10^{12}	tera	T	10^{-3}	milli	*m*
10^{9}	giga	G	10^{-6}	micro	μ
10^{6}	mega	M	10^{-9}	nano	*n*
10^{3}	kilo	k	10^{-12}	pico	*y*
10^{2}	hecto	h	10^{-15}	femto	*f*
10^{1}	deca	da	10^{-18}	atto	α

(G) Permitted Units :

Name	*Symbol*	*Value in S.I. units*
minute	min	1 min = 60 s (**Note.** s also expressed as sec., in the text)
hour	*h*	1 h = 60 min = 3600 s
day	*d*	1 d = 24 h = 86,400 s
degree	°	1° = (π/180) rad
minute	′	1′ = (1/60)° = (π/10,800) rad
second	″	1″ = (1/60)′ = (π/648,000) rad
litre	*l*	1 l = 1d m^3 = 10^{-3} m^3
tonne	*t*	1 *t* = 10^3 kg.

N.B. The information gives the base units in the International System (S.I.) and lists also a number of units derived from them, all of which form a coherent measurement system. In a coherent system, calculations involving a number of quantities may be made and the correct result obtained without the introduction of arbitrary constants.

(H) Temporarily accepted units :

Name	*Symbol*	*Value in S.I.*
nautical mile	—	1 nautical mile = 1852 m
knot	—	1 nautical mile per hour = (1852/3600) m/sec.
are	a	1 a = 1 da m^2 = 10^2 m^2
hectare	ha	1 ha = 1 h m^2 = 10^4 m^2
barn	b	1 b = 100 fm^2 = 10^{-28} m^2
bar	bar	1 bar = 0.1 MPa = 10^5 Pa
standard atmosphere	atm	1 atm = 1013,25 Pa
carat	c	1 c = 200 mg
quintal	q	1 q = 100 kg

1.2. Scope

Thermodynamics, (That branch of science which deals with energy and its transformation), heat transfer and fluid flow are the basic principles underlying refrigeration and air conditioning practice. While the specific treatment of various topics is discussed at appropriate levels in the textbook this chapter is devoted to basic properties and principles of thermodynamics for the purpose of review of the previous knowledge.

1.3. State

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

1.4. Properties

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 constitutes 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.*

1.5. Specific Weight, w_s

It is also known as the weight density. It is the weight per unit volume. It may be expressed in kgf/m^3 in MKS units and Newton/m^3 in SI units and depends upon both the density of the substance and value of the gravitational acceleration g. Let w represent the weight corresponding to certain mass m ; then

$$w = \frac{1}{g_c} \cdot mg \qquad ...(1.1)$$

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 / in SI units.

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

$$w_s = \rho \frac{g}{g_c} \qquad [because\ m = \rho\ V] \qquad ...(1.2)$$

where w_s is the weight density and ρ is the mass density. For example, if the density of water at 22° C is the 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. It may be noted that w_s is the force per unit volume, whereas ρ is the mass per unit volume. The unit 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 unit $g_c \cong 9.81 \frac{\text{kgm}}{\text{kgf.sec}^2}$ and in SI units g_c = 1 kgm/N. sec^2. Thus in SI units $w_s = \rho g$ N/m^3, where ρ is expressed in kg/m^3.

1.6. Specific Volume

It's defined as the volume per unit mass and may be expressed in m^3/kg. It is reciprocal of the density,

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

where υ is the specific volume.

$$1 \text{ kgf} = 9.80665 \text{ N}, \ 1 \text{ kgf/m}^3 = 9.80665 \text{ N/m}^3.$$

1.7. Pressure

The pressure exerted by a system is the force exerted normal to a unit area of the boundary.

The standard atmospheric pressure is defined as the pressure produced by a column of mercury 760 mm high, the mercury density being 13.5951 g/cm^3 and the acceleration due to gravity being its standard value of 980.665 cm/sec^2. The standard atmospheric pressure is 1.0332 kgf/cm^2 and is denoted by *atm*. In SI units it is expressed in N/m^2 or Pascal abbreviated as Pa. Pascal being small normally kilo-pascal (kPa) or Megapascal (MPa) is used. Standard atmosphere pressure is 101325 Pa = 101.325 kPa. = 1.01325×10^5 *Pa* = 1 bar. The unit of bar for pressure is extensively used. Standard Atmospheric pressure = 1.01325 bar.

1 kgf/cm^2 is also called technical atmosphere and denoted by *ata*. It is worth noting that :

1 atm ≅ 101.325 kPa. 1 atm ≈ 760 mm Hg ; 1 bar (= 10^5 N/m^2) ≅ 750 mm Hg ;

1 *ata* = 736 mm Hg 1 mm Hg is also denoted by 1 torr.

Thermodynamic investigations are more concerned with the values of absolute pressure, rather than those of gauge pressure. Conversion from gauge pressure to absolute pressure is done by the relation

$$p_{abs} = p_{gauge} + p_{atmospheric} \quad ...(1.3)$$

(**Note.** 1 kgf/cm^2 abs may be denoted as 1 ata.)

Fig. 1.1 shows schematically this relationship. The datum for absolute pressure is a perfect vacuum, datum for gauge pressure is atmospheric pressure.

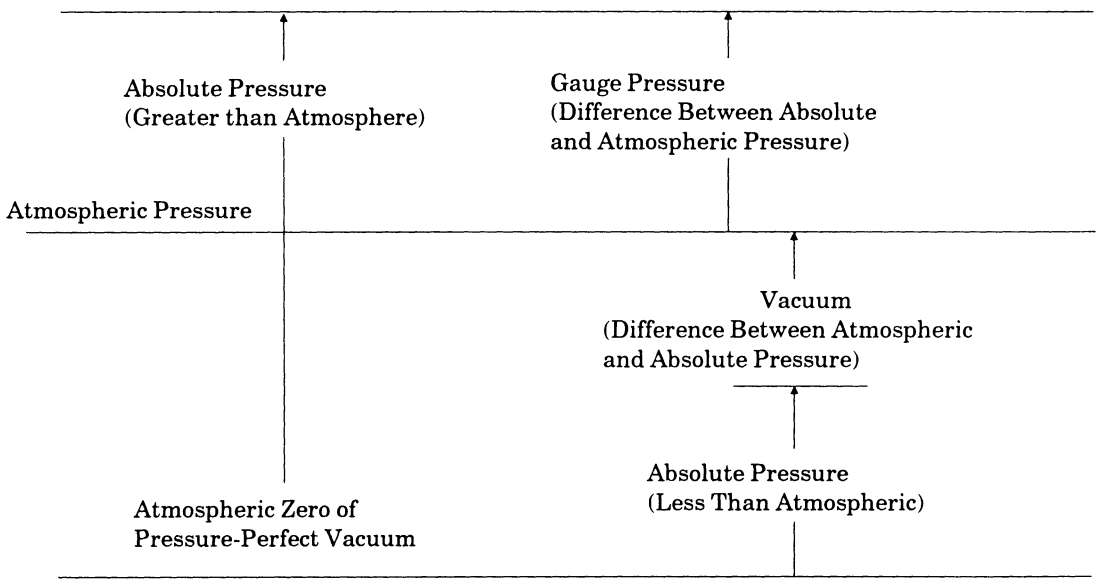


Fig. 1.1. Pressure relationship.

Table 1.1. Conversion Factors for Pressure

	bar	*dyne/cm^2*	*kgf/cm^2 ata*	*N/m^2 or Pa*	*mm Hg (21°C) or torr*	*mm H_2O (21°C)*	*atm*
1 bar =	1	10^6	1.01972	10^5	750.062	10197.2	0.986923
1 dyne/cm^2 =	10^{-6}	1	1.01972×10^{-6}	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
1 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}	1.333223×10^3	10.3595×10^{-3}	1.333223×10^2	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	1.01325×10^6	1.03323	1.01325×10^5	760	10332.3	1

In dealing with fluid flow problems, various types of pressures are commonly used. Static pressure is the pressure sensed by a measuring device, if it were moving with the same velocity as the fluid stream. Impact pressure is the force per unit area perpendicular to the direction of flow when the fluid is brought reversibly to rest. For a constant density fluid, the impact pressure is given by

$$p_{impact} = \frac{\rho V^2}{2g_c} + p_{static}$$

where ρ is the fluid density, V is the velocity. The difference between the impact pressure and the static pressure is due to the velocity and this difference is, therefore, called *velocity pressure*, $\rho V^2/2g_c$. Fig. 1.2 shows the different types of pressures.

In MKS units $g_c = 9.81 \dfrac{\text{kgm}^2}{\text{kgf.sec}^2}$; In SI unit $g_c = 1 \dfrac{\text{kgm}}{\text{N sec}^2}$

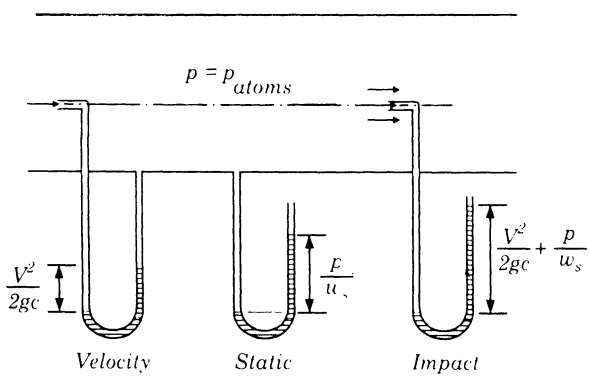


Fig. 1.2. Types of pressure.

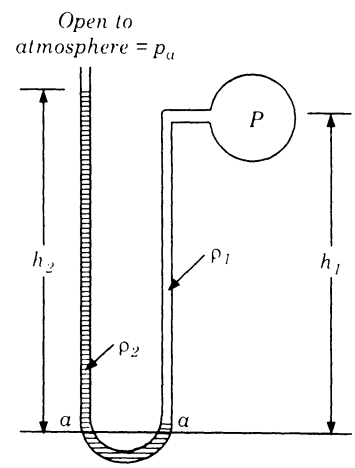


Fig. 1.3. Measuring pressure by manometer.

In fluid flow through a duct, static conditions prevail at the walls of the duct. The velocity at the walls is zero and, therefore, the pressure measured at the wall is the static pressure. If the fluid particles move parallel to the centre line of the duct, the static pressure is uniform across any section of the duct.

To measure pressure slightly different from atmospheric, a nanometer is normally used and the pressure is determined according to the hydrostatic formula. The manometer liquid may be mercury, water, alcohol, etc. A typical manometer is shown in Fig. 1.3. Since the manometer fluid is in equilibrium, the pressure along a horizontal line aa manometer. Then,

$$p + \rho_1 h_1 \frac{g}{g_c} = p_a \rho_2 h_2 \frac{g}{g_c} \qquad ...(1.4)$$

where p is the absolute pressure in the bulb, p_a is the atmospheric pressure exerted on the liquid free surface and ρ_1, ρ_2 are the densities of the liquid in the bulb and the manometer respectively.

ρ_1 is very very small as compared to ρ_2.

$$\therefore \qquad p - p_a = \rho_2 h_2 \frac{g}{g_c} = p_2 h_2 \text{ (if } g = g_c \text{ numerically)} \qquad ...(1.5)$$

1.8. 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.

1.9. 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 the end of a cyclic process.

1.10. Quasi-static Process

If a process is carried out in 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 (Fig. 1.4) *AB* is a quasi-static process at the successive state, for example, at 1, 2, 3 etc. the system is very nearly in thermodynamic equilibrium.

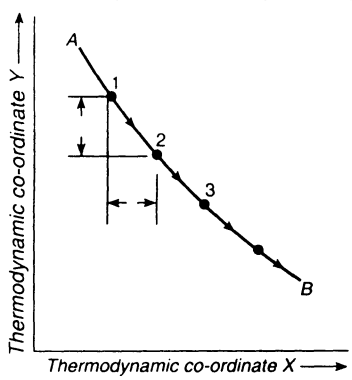


Fig. 1.4

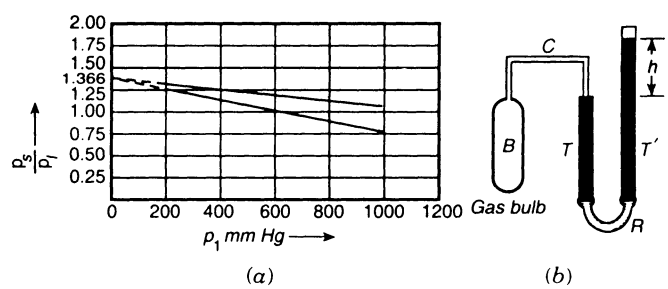


Fig. 1.5

1.11. Standard Scale of Temperature

A scale may be developed which is independent of the properties of a substance.

This can be done as follows with the help of constant volume gas thermometer system (Fig. 1.5).

B is gas bulb.

D is the capillary tube connecting gas bulb to U-tube.

T-T′ is the U-tube formed by two limbs *T* and *T′* and the pipe.

R is the flexible hose pipe.

The gas volume in the gas bulb is kept constant by adjusting the level of mercury in limb *T* at the tip of the capillary. This can be achieved by raising or lowering the limb *T′*. The difference in height *h* of mercury gives the gauge pressure on the gas in bulb *B*.

Let the bulb be kept initially at ice point and the pressure is p_I which is equivalent to say 1000 mm Hg. The bulb is then brought to steam point and pressure observed is p_s. Let this ratio p_s/p_I be determined and called $\left(\frac{p_s}{p_I}\right)_{1000}$. Some gas is then withdrawn such that ice point may be obtained say at 900 mm Hg. In the same way as before $\left(\frac{p_s}{p_I}\right)_{900}$ is obtained. This may

be repeated for more values of p_I. It is important to note that the values of $\frac{p_s}{p_I}$ plotted against p_I are straight lines for all gases such as hydrogen, helium, oxygen, nitrogen etc. and also when these lines are extrapolated, they give a value of $\frac{p_s}{p_I} = 1.366$ (Exact value is 1.366086) at $p_I = 0$.

Thus $$\frac{T_s}{T_I} = \lim_{p_1 \to 0} \frac{p_s}{p_I} = 1.366086 \quad ...(i)$$

Also $$T_s - T_I = 100 \quad ...(ii)$$

These equations define Kelvin or Absolute Centigrade scale and are independent of the properties of individual substance.

Solving equations (*i*) and (*ii*), we get

$$T_s = 373.16°\text{K}$$
$$T_I = 273.16°\text{K}$$
$$T°\text{K} = t° + 273.16$$
$$\cong t°\text{C} + 273$$

And in general for the other temperatures

$$\frac{T}{T_I} = \lim_{p_1 \to 0} \frac{p}{p_I} \quad ...(1.6)$$

Thus T is established uniquely, since T_I is known.

1.12. 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 transition 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 (*iii*) Electricity etc.

1.13. 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 $$F \propto m \cdot g$$
$$= \frac{1}{g_c} \cdot mg = \frac{m}{g_c} \cdot g$$

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

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

$$= \mathbf{\frac{m}{g_c} \cdot g\,Z} \quad ...(1.7)$$

Metric Units :

Express m in kg, g_c in kg m/kgf sec^2, g in m/sec^2 and Z in m.

Thus $\frac{m}{g_c} . gZ$ can be expressed in $\frac{\text{kg} \times \text{kgf sec}^2}{\text{kg m}} \times \frac{m}{\text{sec}^2} \times \text{m}$

$= \text{kgf. m}$

S.I. Units :

Express m in kg. g_c in kg m/ N sec^2 and Z in m

Thus $\frac{m}{g_c} . g\,Z$ can be expressed as

$$\frac{\text{kg} \times \text{N sec}^2}{\text{kg m}} . \frac{\text{m}}{\text{sec}^2} \times \text{m} = \text{N . m or Joule}$$

Also $g_c = 9.81$ in metric unit

and $g_c = 1$ in S.I. units

Thus kgf m = 9.81 N-m.

1.14. 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 $$F = \frac{m}{g_c} . \frac{dV}{dt}$$

and $$\text{Work} = F\,dx = \frac{m}{g_c} . \frac{dV}{d_c} dx = \frac{m}{g_c} . \frac{dx}{dt} . dV$$

or $$\text{Work} = \int_0^x F\,dx = \int_0^V \frac{m}{g_c} . \frac{dx}{dt} dV = \text{Kinetic energy}$$

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

Thus $$\text{K.E.} = \frac{1}{2} \frac{m}{g_c} V^2 \qquad ...(1.8)$$

for $$g_c = 1 \frac{\text{kg m}}{\text{N-sec}^2} \text{ in S.I. units}$$

$$\text{K.E.} = \frac{1}{2} m\,V^2 \text{ N-m or Joule} \qquad ...[1.8\ (a)]$$

for $$g_c = 9.81 \frac{\text{kg m}}{\text{kgf-sec}^2} \text{ in metric units}$$

$$\text{K.E.} = \frac{1}{2} \frac{m}{9.81} V^2 \text{ kgf-m} \qquad ...[1.8\ (b)]$$

(m is expressed in kg., V is expressed in m/sec)

Also $$1 \text{ N-m} = (1 \text{ kg-m/ sec}^2)\ (1\text{m}) = 1\text{kg-m}^2/\text{sec}^2$$

$$1 \text{ kgf-m} = (1 \text{ kg} \times 9.81 \text{ m/sec}^2)\ (1 \text{ m})$$

$$= 9.81 \text{ kg-m}^2/\text{sec}^2.$$

1.15. 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. The different phrases used in the definition required explanation. When a system is considered for macroscopic study, the manner in which a process takes place within the system is of no consequence. Only the energy transfer across the system boundary is of significance.

Therefore, the effect of the energy in transition should be felt external to the system boundary. And this effect could be reduced to only the rise of a weight.

Let us consider a system comprising a battery and a motor as shown in Fig. 1.6.

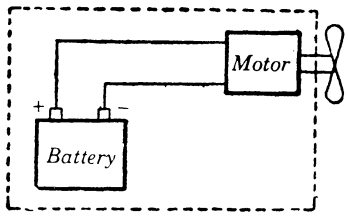


Fig. 1.6

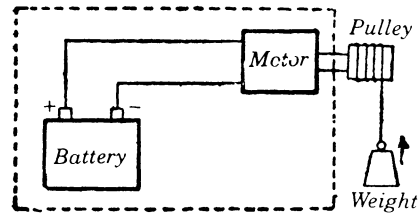


Fig. 1.7

The motor may drive a fan. Thus the effect of the work transfer from the system boundary is the driving of the tan. In order to satisfy the definition fully, it should be possible to reduce this effect to only the rise of a weight. If the fan is replaced by a pulley and weight arrangement shown in Fig. 1.7 the turning of motor will raise the weight and that the sole effect is the raising of weight. Thus, for system of Fig. 1.6, the sole effect external to the system can be reduced to the rise of weight and the work is thus transferred from the system. Let us consider a system as shown in Fig. 1.8. The system boundaries have been changed to exclude the motor. In this case, the flow of electricity takes place across the boundaries. If the motor on bearings is idealised to have 100% efficiency, the sole effect of the transfer of electrical energy external to the system is the rising of a weight. Thus flow of electrical energy across the boundary of the system shown in Fig. 1.8 constitutes work.

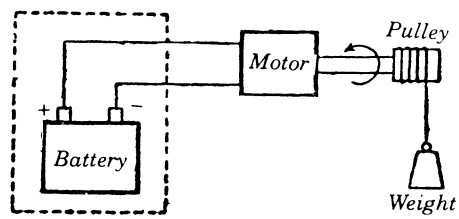


Fig. 1.8

1.16. Work done during a Quasi-static or Quasi equilibrium 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 (Fig. 1.9).

Total force on the piston $F = p.A$,

where p is the pressure of fluid and A is the area of piston.

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

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

where V is the volume.

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. 1.9 or by an equation. Consider the graph in Fig. 1.9, 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.

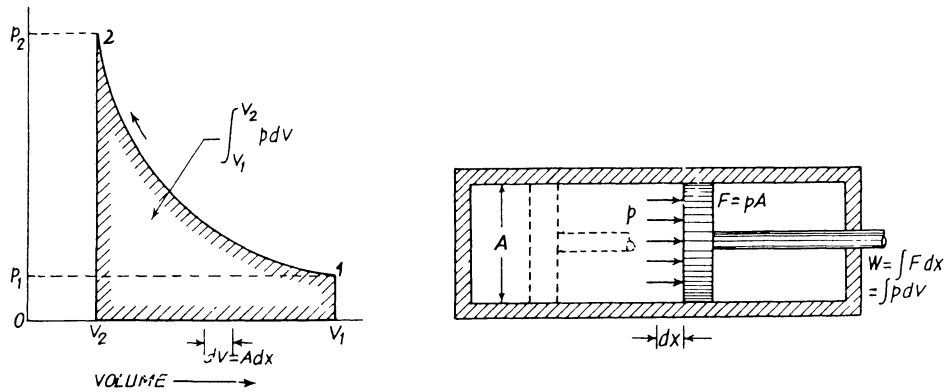


Fig. 1.9

Thus work done on the system

$$ {}_1W_2 = \int_1^2 \delta W = \int_{V_1}^{V_2} p\, dV \qquad ...(1.9) $$

And it is clear that the work done during this quasi-static process in the area under curve shown in Fig. 1.9.

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 $\int p\, dV$ is the work done during a quasi-static process for only a non-flow system. For unit mass it can be written as $\int pdv$, where v is the specific volume.

1.17. pdV Work, a Path Function [Fig. 1.10 (*a*), (*b*), (*c*) and (*d*)]

Since many problems in thermodynamics involve the use of the equation it is convenient to represent equation $\delta W = p\,.\,dV$ graphically.

$$ \delta W = p.dV $$

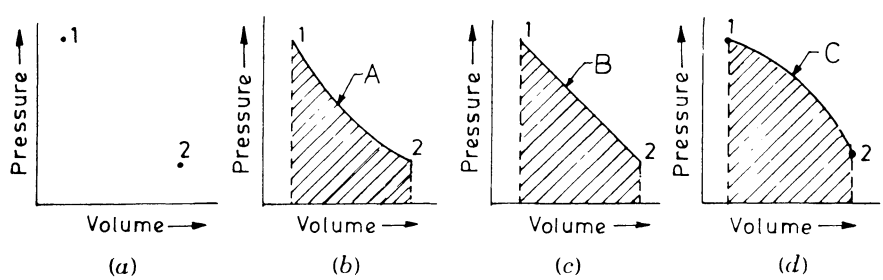


Fig. 1.10

Let us consider state 1 and state 2 as shown on the pV plane in Fig. 1.10 (a). It is possible to go from state 1 to state 2 by many different quasi-static paths as shown in Fig. 1.10 (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 or in mathematical parlance δW is an in-exact differential. In general a quasi-static process may be represented by an equation of the form pV^n = constant, where the index n may have value from $-\infty$ to $+\infty$. Such a process, is often called polytropic process. Fig. 1.11 shows a few typical cases of the polytropic process. For $n = 0$, we have $pV^\circ = p$ = constant (Isobaric process) for $n = 1$, we have pV = constant (Isothermal process) and for $n = \propto$ we have $pV^\propto = C$ or $p^{1/\propto} V = c_1$, or $p^\circ V = V$ = constant (Isometric process).

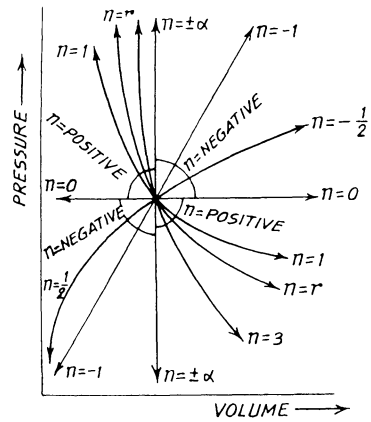


Fig. 1.11

1.18. Limitations of the use of $\int$ pdV

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

(i) The system is a closed one and the process takes place in 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

$$\int \delta w = \int p\, dv.$$

1.19. Flow Work (Fig. 1.12)

A further form of energy transition as a 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 existing in the fluid or region. The concept might be developed by reference to Fig. 1.12. Hence 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 pass 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

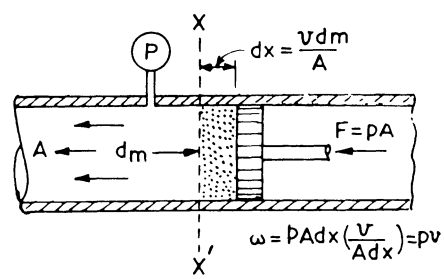


Fig. 1.12

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

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

$$dx = \frac{dV}{A} \qquad ...(1.10)$$

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 of fluid entering becomes

$$w_{flow} \text{ (per unit mass)} = \frac{p\,Adx}{dm} \qquad ...(1.11)$$

$$= \frac{(pA)\,dV/A}{dm} = p\,\frac{dV}{dm} = p\,v \qquad ...(1.12)$$

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.

1.20. 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 that 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 by Q and its units in metric systems are kcal. In SI units it is expressed in Joules abbreviated as J.

Also 1 kcal = 4186.8 J = 4.1868 kJ

1 kJ = 0.2388 kcal.

Heat flow rate is expressed as kcal/hr in MKS units and Watts or J/sec in SI units. Also,

1 kcal/hr = 1.163 J/sec = 1.163 watt. (watt sec)

1 watt = 0.86 kcal/hr.

1.21. Specific heat

The heat required by a unit mass of a substance to raise 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

$d\,t$ = rise in temperature.

We have $$C_n = \lim_{\Delta t \to 0} \frac{\Delta Q}{m\,\Delta t} = \lim_{\Delta t \to 0} \frac{\Delta q}{\Delta t} = \frac{\delta q}{d\,t}$$

or $$\delta q = C_n\,d\,t$$

or $$\delta Q = m\, C_n\, d\, t \qquad ...(1.13)$$

Therefore, $$_1Q_2 = \int_1^2 m\, C_n\, d\, t \qquad ...(1.14)$$

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.

Specific heat $$C_p = \left(\frac{\delta q}{\delta t}\right)_p \text{ at constant pressure} \qquad ...(1.15)$$

and specific heat $$C_v = \left(\frac{\delta q}{\delta t}\right)_v \text{ at constant volume} \qquad ...(1.16)$$

Units for specific heat follow from the definition, *i.e.* kcal/kg °C in MKS units and J/kg °K in SI units. Also

$$\frac{\text{kcal}}{\text{kg°K}} = 4186.8\,\frac{\text{J}}{\text{kg°K}} = 4.1868\,\frac{\text{kilo Joules}}{\text{kg°K}}$$

$$1 \text{ kJ/kg°K} = 0.2388 \text{ kcal/kg °K}$$

$$\cong 0.24 \text{ kcal/kg °K.}$$

It may be interesting to note that numerical value of specific heat in all units except SI units is the same.

$$\frac{\text{BTU}}{\text{1b°F}} = \frac{\text{CHU}}{\text{1b°C}} = \frac{\text{kcal}}{\text{kg°C}}$$

$$C_p = \begin{cases} 1.0 \text{ kJ/kg °K} = 0.239 \text{ kcal/kg °K for dry air} \\ 4.1868 \text{ kJ/kg °K} = 1.0 \text{ kcal/kg/°K for liquid water} \\ 1.88 \text{ kJ/kg °K} = 0.45 \text{ kcal/kg °K for vapour.} \end{cases}$$

1.22. (a) Heat—A Path Function

The equation for heat transfer is given by

$$_1Q_2 = \int_{T_1}^{T_2} m\, C_n\, dt \qquad ...(1.17)$$

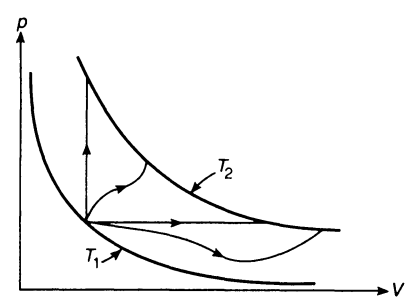


Fig. 1.13

Integration of equation (1.17) will depend upon how temperature T_1 changed to T_2. Fig. 1.13, shows two constant temperature lines on the p-V plane. It is clear that there are many ways for the system to change its temperature from T_1 to T_2. A little thought will reveal that the specific heat C_n may thus have any value, depending upon the process under-gone by the system. $C_n = C_p$ for constant pressure process and $C_n = C_v$ for constant volume process.

1.22. (b) Comparison of Heat and Work

There are many similarities between Heat and Work.

(*i*) Heat and Work are both transient phenomenon. Systems never possess heat or work, but either or both cross system boundaries, when a system undergoes a change of state.

(*ii*) Both heat and work are boundary phenomenon. Both are observed only at the boundaries of the system and both represent energy crossing the boundaries of the system.

(*iii*) Both heat and work are path functions and in-exact differentials.

SI unit of work is Newton-metre (N.m) or Joule (J)

$$1 \text{ N-m} = 1 \text{ J} = (1 \text{ kg/sec}^2)\,(1 \text{ m}) = 1 \text{ kg m}^2/\text{sec}^2$$
$$1 \text{ erg} = 1 \text{ dyne-cm} = (10^{-5} \text{ N})\,(10^{-2} \text{ m}) = 10^{-7} \text{ N-m}$$
$$= 10^{-7} \text{ J}$$
$$1 \text{ kcal} = 427 \text{ kgfm} = 427 \times (9.80665\text{N}) \times \text{m}$$
$$= 41{,}868 \text{ N-m or J} = 4.1868 \text{ kJ}$$
$$1 \text{ kcal} = 4.1868 \text{ kJ} = 3.968 \text{ BTU}$$
$$1 \text{ kJ} = 0.948 \text{ Btu} = 0.239 \text{ kcal}$$
$$1 \text{ Btu} = 0.252 \text{ kcal} = 1.055 \text{ kJ}.$$

1.22. (c) 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.

1.23. Pure Substance—Thermodynamic State

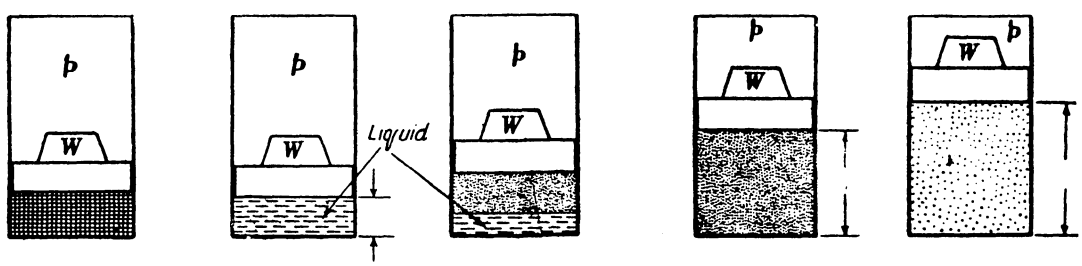
In general a pure substance exists in the following three forms :

(*i*) Solid phase ; (*ii*) Liquid phase ; (*iii*) Vapour or gaseous phase.

Under certain conditions, all these three phases may co-exist. The co-existance of two phases is very common. Water is taken as an illustrative pure substance. When ice melts there is a transformation of phase from solid to liquid. This is called *melting* or *fusion of ice*. Transformation can take place in the opposite direction *i.e.* from liquid to solid. This is called *freezing* or solidification. Similarly the transformation from the liquid phase to vapour phase is called *vaporization*. The transformation in the opposite direction, *i.e.* from vapour to liquid is called *condensation*.

1.24. Phase Transformation at Constant Pressure

Refer Fig. 1.14. Let the cylinder in Fig. 1.14 (*a*) contains 1 kg of ice under a pressure p bar exerted by a weight W placed on the free frictionless piston. Let us assume that p_1 = 5 bar or 500 kPa and the ice is at a temperature of – 10°C. Then let heat be added continuously. First



(*a*) Solid only (*b*) Liquid only (*c*) Saturated liquid vapour (*d*) Saturated vapour only (*e*) Superheated vapour

Fig. 1.14

the ice gets warmer and its temperature rises as recorded by thermometer till the temperature little lower than 0°C is reached. The freezing temperature of water decrease slightly with pressure, being 0°C at standard atmospheric pressure. The warming up process is shown by *AB* in Fig. 1.15. After this the ice begins to melt and a two phase mixture of ice and water remains at the same temperature. No rise in temperature is recorded while heat is being added. This is shown by *BC* in Fig. 1.15. At point *C*, all the ice has melted and we have only one phase,

i.e. liquid water under the same pressure of 5 bar as shown in Fig. 1.14 (*b*). The quantity of heat required to transform ice into water while there is no change of temperature is called heat of fusion. The freezing point, as experimentally found out is a function of pressure, decreasing with an increase in pressure. If heat is further added to water, its temperature starts rising again and continues to do so till the water reaches the temperature of vaporization or boiling. This process is represented in Fig. 1.15 by line *CD*. The boiling temperature is again a function of pressure, its value being 100°C at standard atmospheric pressure. At 5 bar or 0.5 MPa it boils at 151.84°C. This temperature is called the saturation temperature for the stated pressure. It can also be said that at 151.84°C, the saturation pressure of water is 5 bar or 0.5 MPa. After water has reached the saturation temperature, it starts vaporising while temperature remains same and once again we get a two-phase mixture of water and water vapour as shown in Fig. 1.14 (*c*). The two-phase system cannot be defined only by its pressure and temperature. Pressure and temperature are not independent variables. If pressure is known, the corresponding temperature of the two phase system is known. Thus the state of vapour is defined by either the pressure or temperature and the quality x, *i.e.* the fraction of vapour in the whole mass.

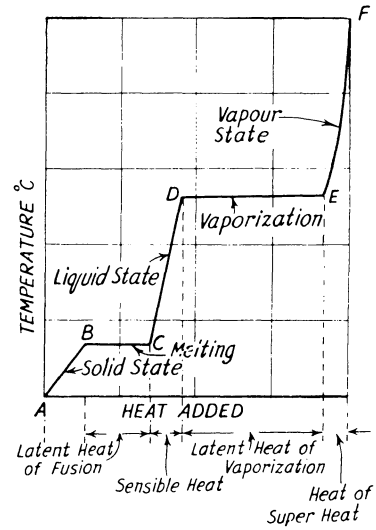


Fig. 1.15

The quality is the percentage of mass that is vapour. This process of vaporization is represented by line *DE*. At point *E*, all the water has vaporised and saturated vapour at pressure p = 5 bar is obtained as shown in Fig. 1.14 (*d*). And the heat required to vaporise the liquid to vapour at constant temperature is known as the latent heat of vaporization or enthalpy of vaporisation.

On further heating, *i.e.* heating after the quality of the vapour is 100%, a further rise in temperature is recorded by the temperature thermometer and the volume will also increase as shown in Fig. 1.14 (*e*). The vapour is said to be superheated. Therefore, superheated vapour is vapour at any temperature above the saturation temperature.

1.25. Summary of Notations Used

The following notations are used to specify the various properties and property changes :

p_i denotes pressure at freezing or during solidification.

p_s denotes pressure at saturation temperature of liquid and vapour or during vaporisation.

p_{sup} denotes pressure of superheated vapour.

Note. Pressure is normally expressed in bar (bar = 10^5 N/m^2)

T_i denotes temperature at freezing or during solidification.

T_s denotes temperature at saturation of liquid and vapour and during vaporisation.

T_{sup} denotes pressure of superheated vapour.

Note. Temperature is normally expressed in °K or °C

v_i denotes specific volume in the solid phase at freezing

v_f denotes specific volume of liquid at saturation temperature

v_g denotes specific volume of vapour at saturation temperature

v_{fg} denotes specific volume change from liquid to vapour at saturation temperature

v_{sup} denotes specific volume of vapour at superheated temperature.

Note. Specific volume is expressed in m^3/kg

u_i denotes specific internal energy of saturated solid

u_f denotes specific internal energy of liquid at saturation temperature

u_g denotes specific internal energy vapour at saturation temperature

u_{fg} denotes specific internal energy change from liquid to vapour at saturation temperature or internal energy of vaporisation.

u_{sup} denotes specific internal energy of superheated vapour.

Note. Specific internal energy is normally expressed in kJ/kg.

h_i denotes specific enthalpy of saturated solid

h_f denotes specific enthalpy of liquid at saturation temperature

h_g denotes specific enthalpy of vapour at saturation temperature

h_{fg} denotes specific enthalpy change of enthalpy from liquid to vapour at saturation temperature or enthalpy of vaporisation.

h_{sup} denotes specific enthalpy of superheated vapour.

Note. Specific enthalpy is normally expressed in kJ/kg.

1.26. Phase Transformation ; p-v-T Data

We have three variables to consider. The procedure adopted, therefore, is to study the variation of one variable with another while the third is kept constant and repeat this for a range of values of the third variable. Let us take unit mass of ice below freezing point enclosed in a cylinder by a piston under a constant load such that the pressure is atmospheric (1 atm = 1.01325 bar). Heat is now applied to the cylinder and pressure remains constant. The temperature rises and there is expansion in ice until the temperature of 0°C or 273.15°K is reached shown by line *AB* in Fig. 1.16.

If the ice is further heated, its temperature remains constant but there is a change of phase shown by *BC*. The change of phase is accompanied by reduction in specific volume. As already stated the heat required during this phase change is called latent heat of fusion denoted by h_{sf} and measured in kJ/kg. After the phase change from solid to liquid is complete, the temperature of liquid rises accompanied by contraction till temperature of about 4°C or 277°K

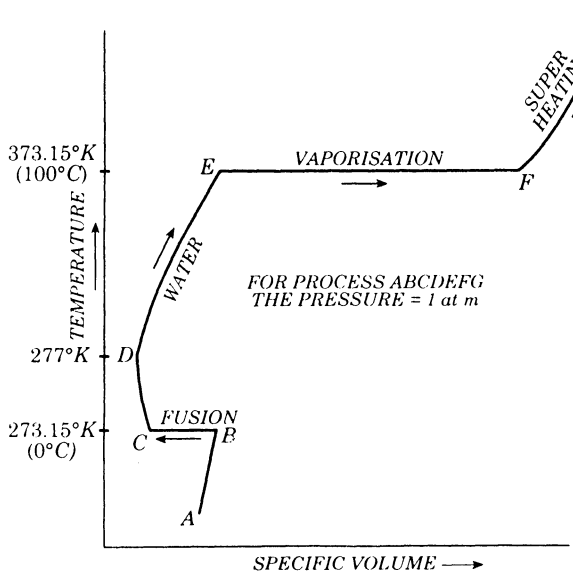


Fig. 1.16

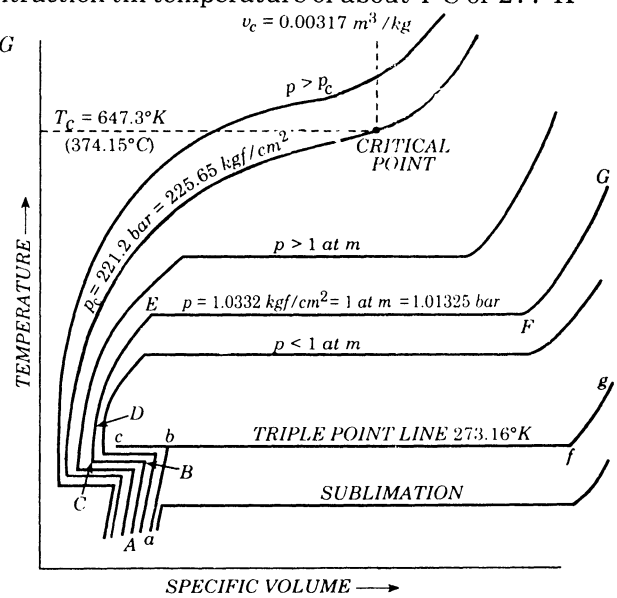


Fig. 1.17

is reached as is shown by point D, and further heating is accompanied by expansion till 100°C or 373.15°K as shown by point E. Heat added accompanied by temperature change is called sensible heat. At point E, again the phase change begins at constant temperature from liquid to vapour.

This is accompanied by large increase in volume until the liquid has completely vaporised as shown at point F. This heat of vaporisation is denoted by h_{fg}. Further heating is again accompanied by change in the temperature and the vapour is said to be superheated, which is again accompanied by expansion in volume.

The same sequence of events may be followed at different pressure as shown in Fig. 1.17. At low pressure there is slight rise in melting points, but a marked drop in boiling points and also very appreciable increase in the change of volume which accompanies evaporation. At a pressure of 0.006112 bar, the melting and boiling temperatures become equal and the change of phase, ice-water-steam is shown by single horizontal line *bcf*. The temperature at which this takes place is 273.16°K and has been accepted internationally as a fixed point for absolute temperature scale. Only at T = 273.16°K and p = 0.006112 bar ice, water and steam co-exist in thermodynamic equilibrium in a closed vessel and *bcf* is called triple point line. At lower pressure than this, ice sublimates to steam.

As the pressure is increased above atmospheric, the change of volume accompanying evaporation decreases, till at sufficiently high pressure, it is zero. This is referred to as the critical point and the properties at this point for water are

$$p_c = 221.2 \text{ bar}$$
$$T_c = 647.3°\text{K} = 374.15°\text{C}$$
$$v_c = 0.00317 \text{ m}^3/\text{kg}.$$

At critical point and above, there is no definite transition from liquid to vapour and phases cannot be distinguished virtually. The latent heat of vaporisation is zero at critical point and has no meaning at pressures higher than critical.

It is quite instructive to show the variation of sublimation melting and boiling on pressure-temperature plane as shown in Fig. 1.18. The formation is obtainable from Fig. 1.17.

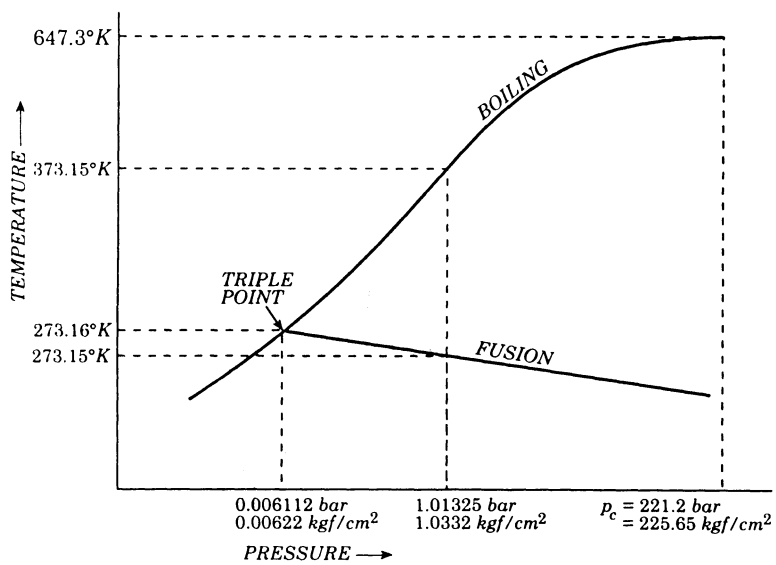


Fig. 1.18

It is often more useful to depict the processes on p-v plane. The same is shown plotted in Fig. 1.19 for liquid vapour phases. Various terms have been introduced to characterise the

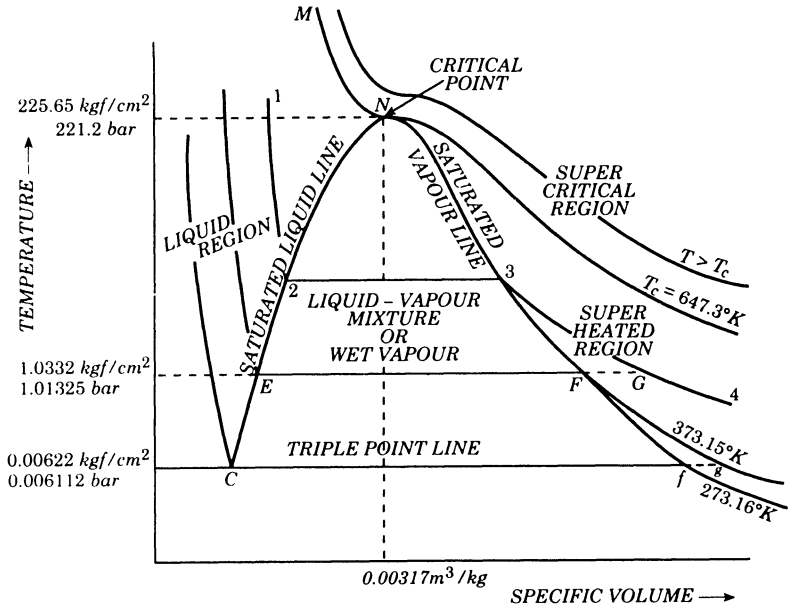


Fig. 1.19

different states through which the substance passes during the expansion 1-2-3-4. From 1 to 2, the water is unsaturated liquid, while at 2 it is saturated liquid. Between 2 and 3, it is two phase mixture of water and vapour or wet vapour. At 3 it is a saturated vapour and from 3 to 4 superheated vapour. All the points representing saturated liquid when joined, form saturated liquid line ; and similarly all the points representing saturated vapour when joined form saturated vapour line. The two lines meet at point, the critical point.

Other Phase Diagrams. For thermodynamic representation of processes and cycles of process, the useful phase diagrams which will be often referred to in this textbook are

(*i*) Pressure-Volume phase diagram.

(*ii*) Temperature-Entropy phase diagram.

(*iii*) Enthalpy-Entropy phase diagram.

(*iv*) Pressure-Enthalpy phase diagram.

Normally the topics discussed and subject-matter presented within the scope of this book deals with properties of substances above triple point. And also the condition involving mixture of solid phase and liquid phase is not dealt with reference to any process in this textbook. Thus most of the charts show properties above triple point and only showing the following states namely (*i*) Liquid phase saturated and sub-cooled (*ii*) Liquid + Vapour (*iii*) Vapour phase, saturated and superheated.

Thus all the phase diagrams are shown diagrammatically from sub-cooled liquid state to superheated vapour state. The diagrams also show the change of state accompanying a constant pressure process above the triple point line.

Constant pressure process showing changes in specific volume are shown by line $v_1 - v_f - v_g - v_{sup}$ on Pressure-Volume diagram (Refer Fig. 1.20).

Constant pressure process showing changes in specific entropy and temperature are shown by line $s_1 - s_f - s_g - s_{sup}$ on Temperature-Entropy-diagram (Fig. 1.21).

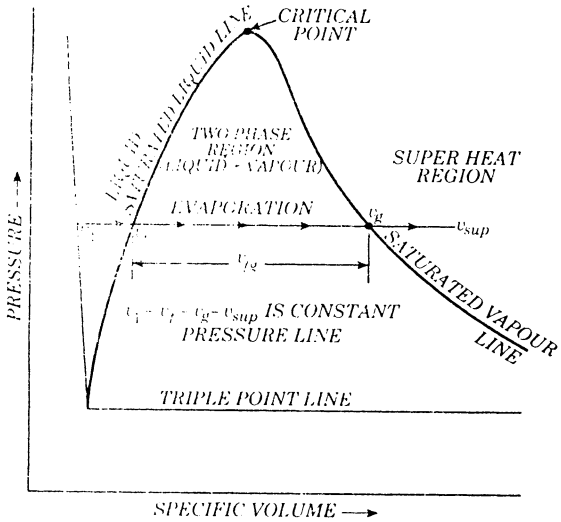


Fig. 1.20

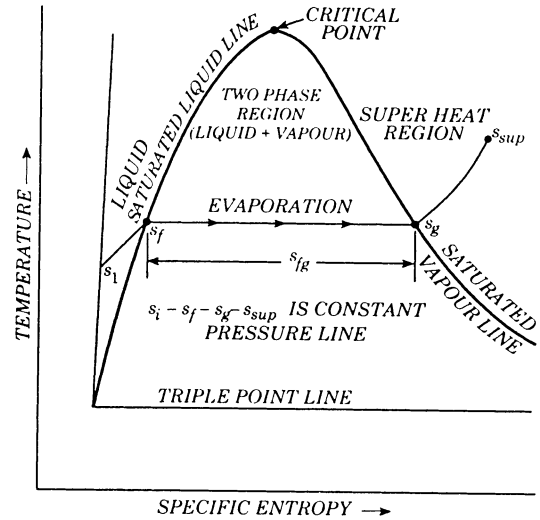


Fig. 1.21

Constant pressure process showing changes in enthalpy and entropy are shown by line $s_1 = s_f = s_g = s_{sup}$ on Enthalpy-Entropy diagram (Fig. 1.22).

Constant pressure process showing changes in enthalpy are shown by line $h_1 = h_f = h_g = h_{sup}$ on Pressure-Enthalpy diagram (Refer Fig. 1.23).

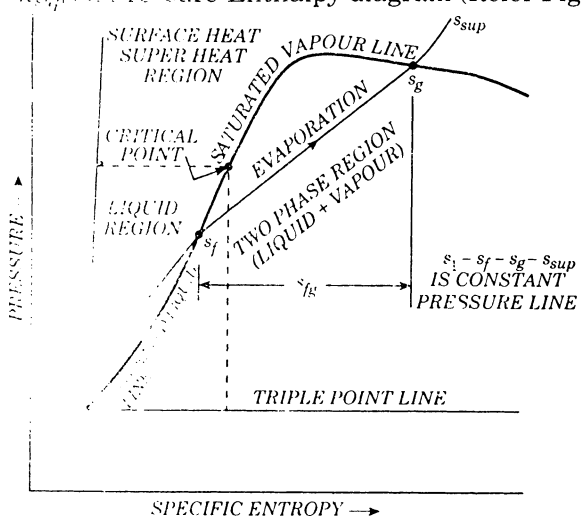


Fig. 1.22

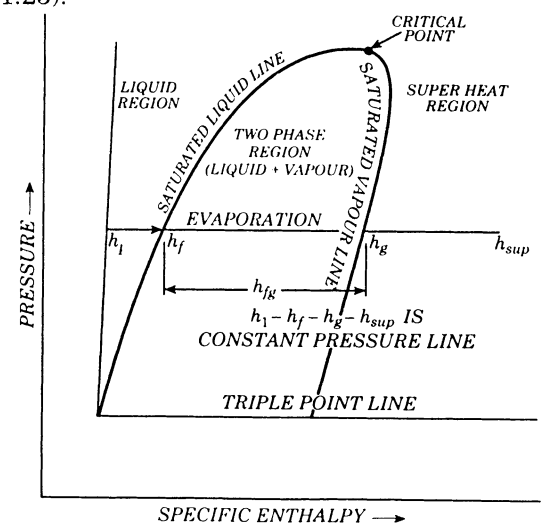


Fig. 1.23

1.27. First Law of Thermodynamics. The first law of thermodynamics can be written as:

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

i.e.
$$\oint \delta Q \propto \oint \delta W \qquad ...(1.18)$$

or
$$\oint \delta Q = \oint \delta W \text{ in consistent units} \qquad ...(1.19)$$

Problem 1.1. *During a cycle comprising of four processes heat transfers are the following : + 60 kJ, – 8 kJ, – 24 kJ and + 6 kJ. Determine the network for the cycle.*

Solution. $\oint \delta Q = 60 - 8 - 24 + 6 = 34$ kJ

Thus $\oint \delta W = \oint QW = 34$ kJ or **34,000 N-m.**

1.28. Energy—Internal Energy

There exists a property of a system called energy, U such that change in its value is the algebraic sum of the heat supplied and the work done during change in state.

This is also called the Corollary 1 of the First Law of Thermodynamics and also be expressed as

$$d\,U = \delta\,Q - W \qquad \text{...(1.20)}$$

Problem 1.2. *A system undergoes a cycle composed of four process 1-2, 2-3, 3-4 and 4-1. The energy transfer are tabulated below.*

Process	*Q (kJ/min)*	*W (kNm/min)*	*Δ U (kJ/min)*
1-2	*400*	*150*	—
2-3	*200*	—	*300*
3-4	*– 200*	—	—
4-1	*0*	*75*	—

(i) Complete the table ; and

(ii) Determine the rate of work in kW.

Solution. For process 1-2,

$$\Delta\,U = {}_1Q_2 - {}_1W_2 = 400 - 150 = 250 \text{ kJ/min}$$

For process 2-3, $\quad {}_2W_3 = {}_2Q_3 - \Delta\,U = 200 - 300 = -100$ kNm/min

For process 4-1, $\quad \Delta U = {}_4Q_1 - {}_4W_1 = 0 - 75 = -75$ kJ/min

Also $\quad \oint dU = 0.$

Therefore, $250 + 300 + \Delta\,U_{3\text{-}4} - 75 = 0$; $\quad$ or $\Delta\,U_{3\text{-}4} = -475$ kJ/min

Now for process 3-4, $\quad {}_3Q_4 = \Delta\,U_{3\text{-}4} + {}_3W_4 = -475 + {}_3W_4$

or $\quad {}_3W_4 = +475 - 200 = 275$ kNm/min

Since $\quad \oint \delta\,Q = \oint \delta\,W$

and net cycle heat transfer $\quad = \oint \delta\,Q$

$= 400 + 200 - 200 + 0 = 400$ kJ per 4 minutes

$= \dfrac{400}{4}$ kJ/min. $= \dfrac{400}{60 \times 4}$ kW = **1.667 kW.**

Problem 1.3. *A system (non-flow) under goes a cycle composed of five process 1-2, 2-3, 3-4, 4-5 and 5-1. The energy transfers are tabulated below :*

Process	*Q kJ/sec or kW*	*W kW or kJ/sec*	*Δ U kJ/sec or kW*
1-2	*0*	*– 5*	—
2-3	*10*	—	*10*
3-4	*5*	*2*	—
4-5	*0*	—	*–10.5*
5-1	—	*0*	—

(i) Complete the table, and $\quad$ *(ii) determine the rate of work in kW.*

Solution. Process 1-2,

$$Q = \Delta U + W$$
$$0 = \Delta U - 5$$
$$\Delta U = +5 \text{ kW}$$

Process 2-3, $10 = 10 + W$ or $W = 0$ kW

Process 3-4, $5 = \Delta U + 2$ or $\Delta U = 3$ kW

Process 4-5, $0 = -10.5 + W$ or $W = +10.5$ kW

Also $\oint dU = 0$

$\therefore$ $+5 + 10 + 3 - 3 - 10.5 + \Delta U_{5-1} = 0$

or $\Delta U_{5-1} = 10.5 - 5 - 10 - 0 = -7.5$ kW

Thus, process 5-1, $Q = 0 + (-7.5) = -7.5$ kW.

Thus table is completed.

Also $\oint \delta Q = \oint \delta W$ and net cyclic heat transfer

$$\int \delta Q = 0 + 10 + 5 + 0 - 7.5 = 7.5 \text{ kW in four seconds.}$$

Therefore, cycle rate of work $= \dfrac{7.5}{4} =$ **1.875 kW.**

1.29. 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 equation for a process according to the First Law of Thermodynamics can be written as

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

Refer Fig. 1.24. It explains the constant volume process. Main characteristic of this process is that displacement work is eliminated. The boundary of the system is rigid. Paddle

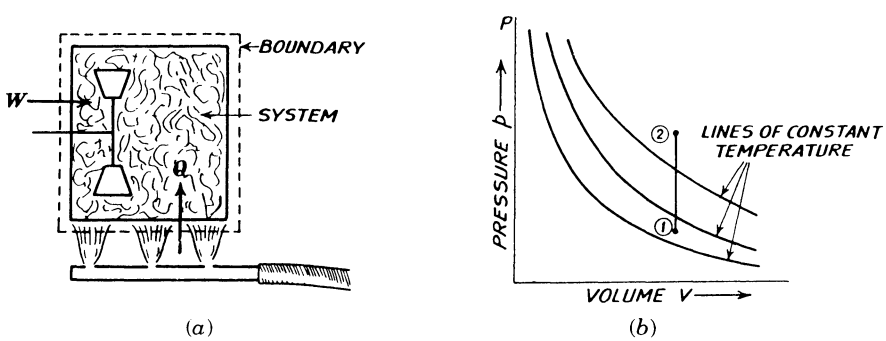


Fig. 1.24

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

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

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 $\delta Q = dU = mC_v\, dT$

or $\delta q = du = C_v dT$ ...(1.22)

or $\left(\dfrac{du}{dT}\right)_v = C_v$ ...(1.23)

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

It is expressed mostly as kJ/kg °K.

(*ii*) **Constant pressure process or Isobaric Process** (Fig. 1.25). In a constant pressure process, the system is subjected to constant hydrostatic pressure at the boundaries.

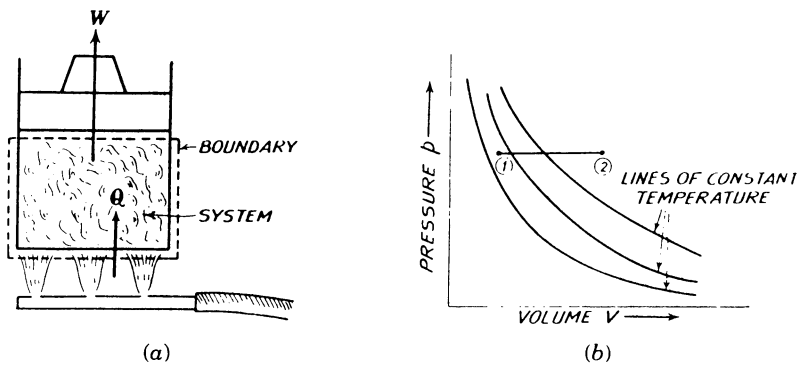


Fig. 1.25

It is illustrated by fluid contained in cylinder and piston with weight 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

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

Since p is constant throughout the process

$$\delta Q = dU + d\,(pV) = d\,(U + pV) = dH \qquad ...(1.24)$$

where H is known as the enthalpy.

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

or $\delta Q = dH = mC_p\, dT$

For unit mass, $\delta q = dh = C_p\, dT$

or $\left(\dfrac{dh}{dT}\right)_p = C_p$ ...(1.25)

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 sides of the equation. Since

right side of equation has each of the quantities as properties, enthalpy is also a property. For unit mass (Specific Enthalpy)

$$h = u + pv \qquad ...(1.26)$$

Specific Enthalpy is mostly expressed in kJ/kg.

(*iii*) **Constant temperature process or Isothermal process** (Fig. 1.26). 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 decreases 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.

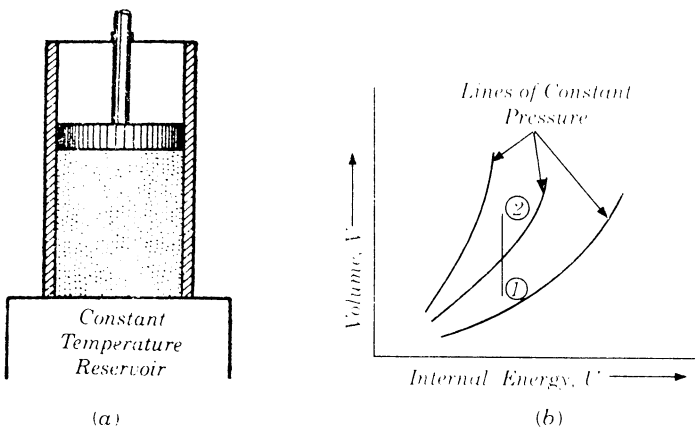


Fig. 1.26

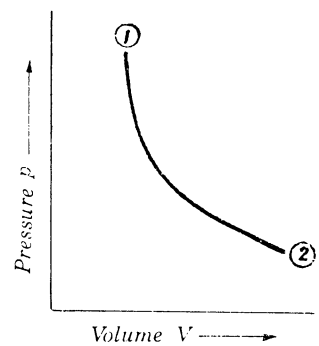


Fig. 1.27

$$\therefore \qquad \delta Q = pdV \text{ (for gas)}$$

or

$$_1Q_2 = \int_1^2 pdV \qquad ...(1.27)$$

(*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 surrounding.

According to First Law of Thermodynamics

$$\delta Q = dU + \delta W. \text{ But } \delta Q = 0$$

Therefore,

$$\delta W = -dU \qquad ...(1.28)$$

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

$$\delta W = -dU = -mC_v\,dT \qquad ...(1.29)$$

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

$$\delta W = pdV$$

or

$$pdV = -dU \qquad ...(1.30)$$

or

$$pdV + dU = 0 \qquad ...(1.31)$$

Therefore,

for a prefect gas $$pdV + mC_v\, dT = 0 \quad ...(1.32)$$

and $$pV = mRT$$

or $$pdV + Vdp = mRdT \quad ...(1.33)$$

for unit mass $$pdv + C_v dT = 0 \quad ...(1.34)$$

and $$pdv + vdp = RdT \quad ...(1.35)$$

Thus $$C_v \left(\frac{pdv + vdp}{R} \right) + p\, dv = 0 \quad ...(1.36)$$

or $$C_v\, (pdv + vdp) + R\, pdv = 0 \quad ...(1.37)$$

or $$C_v\, (pdv + vdp) + pdv(C_p - C_v) = 0 \quad ...(1.38)$$

or $$C_v\, vdp + C_p\, pdv = 0 \quad ...(1.39)$$

or $$\frac{dp}{p} + \frac{C_p}{C_v} \times \frac{dv}{v} = 0 \quad ...(1.40)$$

or $$\log_e p + \gamma \log_e v = \text{constant} = \log_e (\text{constant})$$

Thus $$p\, v^\gamma = C \quad ...(1.41)$$

Fig. 1.17 illustrates the curve given by equation (1.41) on p-v co-ordinates.

Equation (1.41) may also be written in the following forms for the two end states reached during a process

(*i*) $$p_1\, v_1^\gamma = p_2\, v_2^\gamma \quad ...(1.42)$$

(*ii*) $$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1} \right)^{\gamma - 1} \quad ...(1.43)$$

(*iii*) $$\frac{T_1}{T_2} = \left(\frac{p}{p_2} \right)^{(\gamma - 1)/\gamma} \quad ...(1.44)$$

Equation (1.44) also helps in evaluation of pdv work during the process.

Work done during the process per kg of working substances.

$$_1w_2 = \int_{v_1}^{v_2} pdv.$$

But $$pv^\gamma = C$$

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

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

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

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 $$_1w_2 = \frac{p_1\, v_1 - p_2\, v_2}{\gamma - 1} \quad ...(1.45)$$

If p is expressed in N/m^2, v in m^3/kg

or
$$_1w_2 = \frac{p_1 v_1 - p_2 v_2}{\gamma - 1} \text{ Nm/kg or J/kg} \quad ...(1.46)$$

Also
$$_1w_2 = \frac{R(T_1 - T_2)}{\gamma - 1} \text{ Nm/kg or J/kg} \quad ...(1.47)$$

If R *is expressed in* J/kg °K.

(*vi*) **Polytropic reversible process.** Equation (1.41) is very convenient form for the 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 equations can be written by angology to equations for the reversible adiabatic process which is only a special case of polytropic process with $n = \gamma$.

$$p_1 v_1^n = p_2 v_2^n \quad ...(1.48)$$

$$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1}\right)^{n-1} \quad ...(1.49)$$

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{n-1}{n}} \quad ...(1.50)$$

$$_1w_2 = \frac{p_1 v_1 - p_2 v_2}{n - 1} \quad ...(1.51)$$

Thus for unit mass $_1w_2 = \dfrac{p_1 v_1 - p_2 v_2}{n - 1}$

Heat transfer per unit mass

$$_1q_2 = (u_2 - u_1) + \int_1^2 p\,dv \quad ...(1.52)$$

$$= C_v (T_2 - T_1) + \frac{R(T_2 - T_1)}{1 - n} \quad ...(1.53)$$

Table 1.2 Summary of Processes for Perfect Gas for Unit Mass

Processes	*Constant pressure*	*Constant Volume*	*Constant temperature*	*Reversible adiabatic*	*Polytropic*
(1)	(2)	(3)	(4)	(5)	(6)
Index n	$n = 0$	$n = \infty$	$n = 1$	$n = \gamma$	$n = n$
p, v, T relation	$\frac{T_2}{T_1} = \frac{v_2}{v_1}$ (Boyle's Law)	$\frac{T_2}{T_1} = \frac{p_2}{p_1}$	$p_1v_1 = p_2v_2$ (Charles Law)	$p_1v_1^\gamma = p_2v_2^\gamma$ $\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} = \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma}$	$p_1v_1^n = p_2v_2^n$ $\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n-1} = \left(\frac{p_2}{p_1}\right)^{(n-1)/n}$

(1)	(2)	(3)	(4)	(5)	(6)
Heat added kJ/kg	$C_p(T_2 - T_1)$	$C_v(T_2 - T_1)$	$p_1 v_1 \log_e \frac{v_2}{v_1}$	0	$C_n(T_2 - T_1) = C_v\left(\frac{\gamma - n}{1 - n}\right)(T_2 - T_1)$
$\int_1^2 p dv$	$p_1(v_2 - v_1)$	0	$p_1 v_1 \log_e \frac{v_2}{v_1}$	$\frac{p_2 v_2 - p_1 v_1}{1 - \gamma}$	$\frac{p_2 v_2 - p_1 v_1}{1 - n}$
Specific Heat C	C_p	C_v	...	...	$C_n = C_v\left(\frac{\gamma - n}{1 - n}\right) = C_v + \frac{C_p - C_v}{1 - n}$

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

$$= \left[C_v + \frac{(C_p - C_v)}{1 - n}\right](T_2 - T_1)$$

$$_1q_2 = \frac{C_p - n\,C_v}{1 - n}(T_2 - T_1) \qquad ...(1.54)$$

$$= C_n\,(T_2 - T_1) \qquad ...(1.55)$$

where $$C_n = \frac{C_p - n\,C_v}{1 - n} \qquad ...(1.56)$$

or $$C_n = \left(\frac{\gamma - n}{1 - n}\right) C_v$$

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

Thus $$_1q_2 = \left(\frac{\gamma - 1}{1 - n}\right) C_v\,(T_2 - T_1) \qquad ...(1.57)$$

$$= \left(\frac{\gamma - n}{1 - n}\right) C_v \frac{p_2\,v_2 - p_1\,v_1}{R} \qquad ...(1.58)$$

$$= \left(\frac{\gamma - n}{1 - n}\right) C_v \frac{p_2\,v_2 - p_1\,v_1}{C_p - C_v} \qquad ...(1.59)$$

$$= \left(\frac{\gamma - n}{1 - n}\right) C_v \frac{p_2\,v_2 - p_1\,v_1}{C_v\left(\frac{C_p}{C_v} - 1\right)} \qquad ...(1.60)$$

$$= \frac{\gamma - n}{\gamma - 1}\,\frac{p_2\,v_2 - p_1\,v_1}{1 - n} \qquad ...(1.61)$$

$$= \frac{\gamma - n}{\gamma - 1} \times \text{Work done} \qquad ...(1.62)$$

or $$\delta q = \frac{\gamma - n}{\gamma - 1} \cdot p d\,v \qquad ...(1\ 63\ a)$$

or $$q = \frac{\gamma - n}{\gamma - 1}\int p d\,v \qquad ...(1.63\ b)$$

Fig. 1.28 shows number of reversible polytropic processes on the p-v plane. Considering the starting points as (1) fourth quadrant will contain expansion processes and second quadrant will contain compression process. 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 process respectively.

1.30. Flow Process and Control Volume

In most engineering plants, the substance continuously flows in and the out of the component. Fig. 1.29 shows diagrammatically a heating chamber or a boiler, where heat Q is

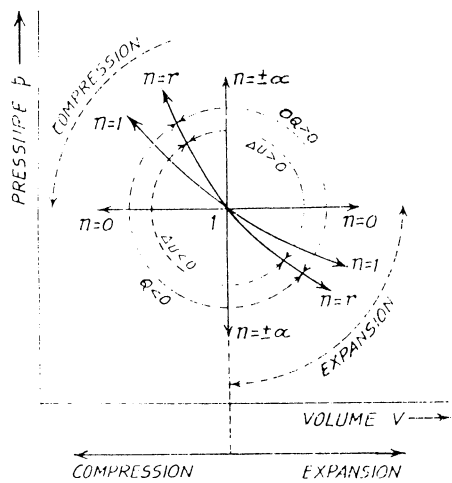


Fig. 1.28

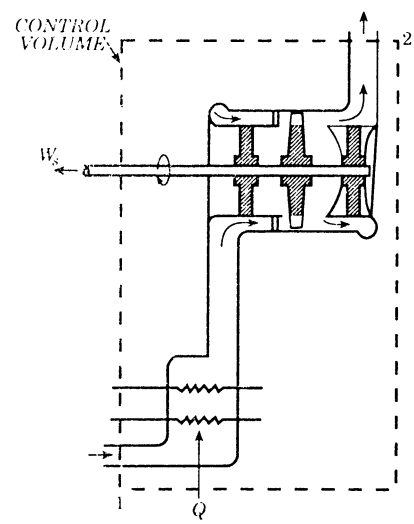


Fig. 1.29

added and 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 applicable. In analysing such process, called flow processes, a concept of control volume is introduced. Imaginary boundaries are put around the component to be studied as shown in Fig. 1.29. The space bounded by these boundaries is called 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.

1.31. 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

$$\left(u_1 + p_1 v_1 + \frac{V_1^2}{2} + g z_1\right) + q = \left(u_1 + p_2 v_2 + \frac{V_2^2}{2} + g z_2\right) + w_s \qquad ...(1.64)$$

or for m mass flow rate, $m\left(u_1 + p_1 v_1 + \frac{V_1^2}{2} + g z_1\right) + {}_1Q_2 = m\left(u_1 + p_2 v_2 + \frac{V_2^2}{2} + g z\right) + W_s$ ...(1.65)

Equation (1.65) is called steady flow energy equation.

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

$$m\left(h_1 + \frac{V_1^2}{2} + g z_1\right) + {}_1Q_2 = m\left(h_2 + \frac{V_2^2}{2} + g z\right) + W_s \quad ...(1.66)$$

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

1.32. Flow Processes

The steady flow energy equation for unit flow is given by (dimensional consistance to be checked when used).

$$h_1 + \frac{V_1^2}{2} + g z_1 + q = h_2 + \frac{V_2^2}{2} + g z_2 + w_s$$

It can also be written in the form

$$dh + d\left(\frac{V^2}{2}\right) + d(g z) = \delta q - \delta w_s \quad ...(1.67)$$

Also $\quad h = u + pv$

Therefore, $\quad dh = du + pdv + vdp \quad ...(1.68)$

Thus $\quad du + pdv + vdp + d\left(\frac{V^2}{2}\right) + d(g z) = \delta q - \delta w_s \quad ...(1.69)$

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,

$$du + pdv = \delta q \quad ...(1.70)$$

i.e. equation (1.70) holds goods for flow as well as a non-flow processes.

Therefore, equation (1.69) gets reduced to,

$$vdp + d\left(\frac{V^2}{2}\right) + d(g z) = -\delta w_s \quad ...(1.71)$$

$$\delta w_s = -vdp - d\left(\frac{V^2}{2}\right) - d(g z) \quad ...(1.72)$$

Therefore, $\quad w_s = -\int_{p_1}^{p_2} vdp - \frac{V_2^2 - V_1^2}{2} - (z_2 - z_1)g \quad ...(1.73)$

If the kinetic energy and potential energy changes are negligible, equation (2.82) reduces to

$$w_s = -\int_{p_1}^{p_2} vdp \quad ...(1.74)$$

1.33. Throttle Process

A process takes place in such a way that the fluid expands from high pressure to low pressure without doing any work, and there is no change in kinetic energy and potential energy of the fluid as also there is no heat transfer. Such a process is called throttling process. Fig. 1.30 illustrates an experimental set up proposed by Joule-Thomson. The experiment is popularly known as Joule-Thomson porous plug experiment.

As stream of gas at higher pressure p_1 flows in through one side of the porous plug completely insulated from the surroundings and comes out of the porous plug at lower pressure p_2.

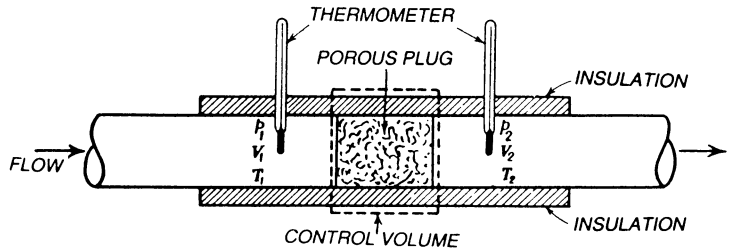


Fig. 1.30

We have

[Energy going into the control volume] – [Energy going out of the control volume]
= [Energy stored in control volume]

But steady flow energy equation is based on the assumption that the state of fluid is the same at the point in control volume or the state of the fluid at any point in a control volume is maintained same. The mass going in is also equal to mass going out. Thus there cannot be any energy stored in control volume.

$\therefore$ (Energy going in) – (Energy going out) = 0

or $$m\left(u_1 + p_1 v_1 + \frac{V_1^2}{2} + g z_1\right) - m\left(u_2 + p_2 v_2 + \frac{V_2^2}{2} + g z_2\right) = 0 \quad ...(1.75)$$

and by our statement of the process, the changes in kinetic and potential energies are neglected. Therefore, we have

$$u_1 + p_1 v_1 = u_2 + p_2 v_2 \quad ...(1.76)$$

or $$h_1 = h_2 \quad ...(1.77)$$

This process has a very wide application in engineering practice. Fig. 1.31 shows one typical application of the throttling process when fluid passes in a pipe line through a partially opened valve. Throttling is an irreversible process. Actually throttling degrades energy and dissipates it in useless turbulence.

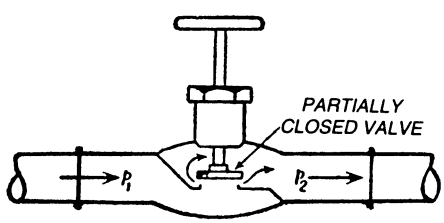


Fig. 1.31

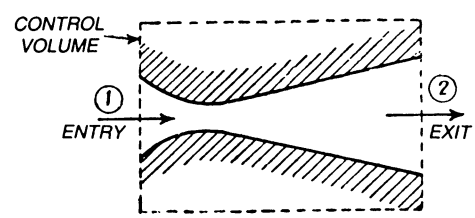


Fig. 1.32

1.34. Applications of Steady Flow Energy Equation

(*i*) **Nozzle.** Nozzle is a contrivance to increase kinetic energy of the flowing substance at the cost of pressure drop. Fig. 1.32 shows a nozzle. This section deals with the nozzles only from the point of view of the application of the steady flow energy equation.

We have $$h_1 + \frac{V_1^2}{2} + g z_1 + q = h_2 + \frac{V_2^2}{2} + g z_2 + w_s$$

The shaft work is obviously zero,

i.e. $$w_s = 0.$$

The nozzles are thermally insulated and are characterised by high rate of the flow of fluids.

Thus, heat transfer is also negligible,

i.e. $$q = 0.$$

The change is elevation between the entry and the exit point is negligible,

i.e. $$(z_2 - z_1) = 0.$$

Therefore, the equation reduces to

$$h_1 + \frac{V_1^2}{2} = h_2 + \frac{V_2^2}{2} \qquad ...(1.78)$$

or $$(V_2^2 - V_1^2) = 2\,(h_1 - h_2) \qquad ...(1.79)$$

(*ii*) **Boiler** (Fig. 1.33). The boiler is characterised by the following features :

(*a*) Velocity change is not appreciable and may be neglected

i.e. $$\frac{V_2^2 - V_1^2}{2} = 0.$$

(*b*) Elevation change between inlet and exit point may also be neglected, *i.e.*

$$(z_2 - z_1) = 0.$$

(*c*) There is not shaft work.

By selecting the control volume, it can be treated as steady flow system and the main function of the boiler is the transfer of heat to the steady flow system.

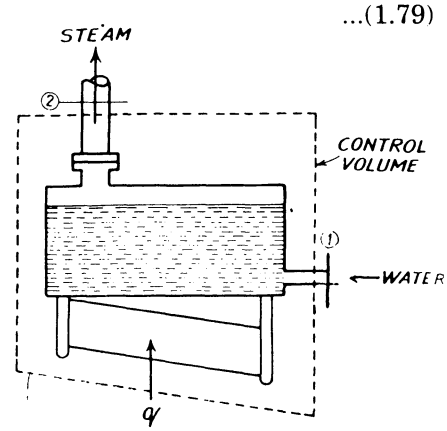


Fig. 1.33

The steady flow energy equation reduces to

$$u_1 + p_1 v_1 + q = u_2 + p_2 v_2$$

$$\therefore \quad q = (u_2 - u_1) + (p_2 v_2 - p_2 v_1)$$

$$\therefore \quad q = (h_2 - h_1) \qquad ...(1.80)$$

(*iii*) **Condenser** (Fig. 1.34). Primary function of a condenser is the transfer of heat out from the steady flow system. In this case there are two steady flow mass streams. It is characterised by

(*a*) No shaft work.

(*b*) No change in kinetic energy.

(*c*) No change in potential energy.

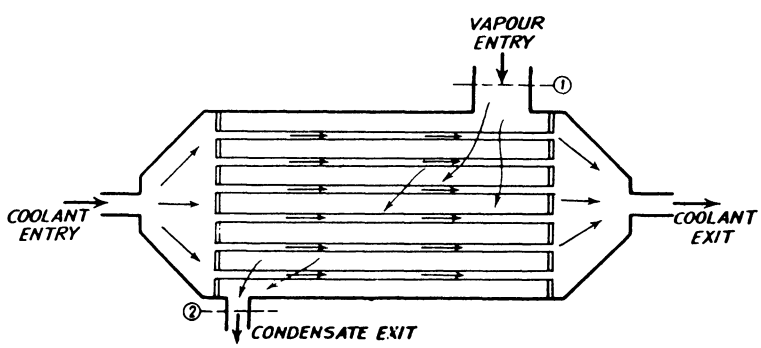


Fig. 1.34

Let m_c = mass rate of coolant flowing
m_v = mass rate of vapour flowing
h_{1c} = enthalpy of coolant at entry
h_{1v} = enthalpy of vapour at entry
h_{2c} = enthalpy of coolant at exit
h_{2v} = enthalpy of vapour at exit

Thus, $$m_c h_{1c} + m_v h_{1v} = m_c h_{2c} + m_v h_{2v} \quad ...(1.81)$$

or, taking only one steady flow stream of vapour and considering heat rejection from the control volume, we have

$$Q = m_v (h_{1v} - h_{2v}) \quad ...(1.82)$$

(*iv*) **Evaporator (In a refrigerator).** Refer Fig. 1.35. Process occurring in evaporator is the reverse of what happen in a condenser. In evaporator liquid enters, receives heat at constant pressure and leaves as vapour. The shaft work, kinetic energy change and the potential energy change are negligible. Thus, we have

$$q = (h_2 - h_1) \quad ...(1.83)$$

where h_2 = enthalpy of refrigerant at exit
h_1 = enthalpy of refrigerant at entry

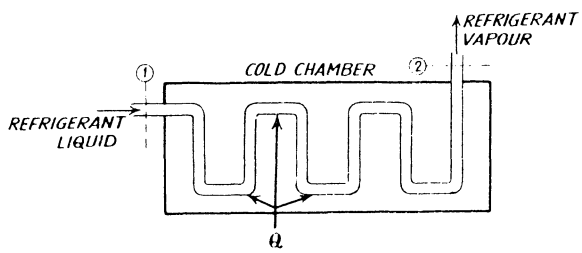


Fig. 1.35

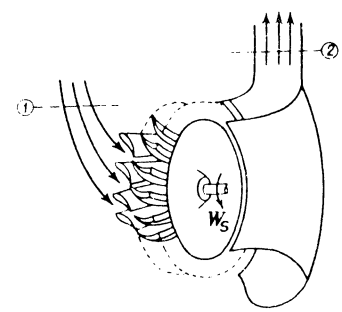


Fig. 1.36

(*v*) **Turbine** (Fig. 1.36). The turbine is characterised by

(*a*) Negligible heat transfer as it is thermally insulated and flow rates are very high.

(*b*) Negligible velocity change in flow of fluid.

(*c*) Negligible potential energy change.

It is a device for obtaining work from a steady flow of fluid expanding from high pressure to lower pressure. Expansion may also be adiabatic due to thermal insulation. Thus, for unit mass rate,

$$\frac{V_2^2 - V_1^2}{2} = 0, (z_2 - z_1) = 0, q = 0$$

or $$h_1 = h_2 + w_s$$

or $$w_s = (h_1 - h_2) \quad ...(1.84)$$

(*vi*) **Rotary compressor.** Here also the flow rates are very high and the process can be treated as adiabatic. It can be treated turbine for the purpose of steady flow process. Here shaft work is done and the fluid is compressed.

Thus $$w_s = (h_1 - h_2) \text{ for unit mass rate} \quad ...(1.85)$$

Here h_2 is greater than h_1 and, therefore, w_s is negative or done on the system/unit mass rate.

(*vii*) **Reciprocating compressor** (Fig. 1.37). The control volume includes the receiver which is of sufficiently large capacity as not to allow any fluctuation of flow in discharge line, the reciprocating compressor may also be treated as a steady flow machine. But due to low rates of flow and large areas in contact with the surroundings besides a deliberate attempt to remove heat to reduce the shaft work done on it, there is appreciable heat transfer involved.

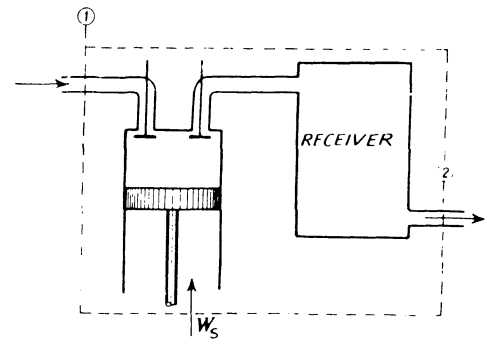


Fig. 1.37

Thus steady flow energy equation for unit mass reduces to

$$w_s = q + (h_1 - h_2) \qquad ...(1.86)$$

Here q is negative and h_2 greater than h_1.

Therefore, w_s is negative or done on the system.

1.35. Second Law of Thermodynamics

(*i*) **Kelvin Planck Statement of Second Law of Thermodynamics.** *It is impossible to construct an engine, which while operating in a cycle, produces no other effect except to extract heat from a single reservoir and do equivalent amount of work.*

Thus cyclic work is possible only with two temperature levels or two temperature reservoirs, and heat is transferred from high temperature level to heat engine and from heat engine to low temperature level.

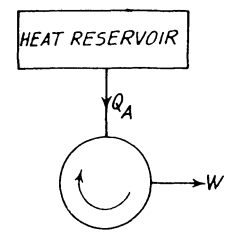


Fig. 1.38

(*ii*) **Perpetual Motion Machine of the Second Kind.** First Law of Thermodynamics does not put any restriction as to the fraction of heat drawn from a heat reservoir that can be converted to work; 100% efficient heat engine does not violate the First Law of Thermodynamics. But the Second Law of Thermodynamics expresses the fact that a heat engine must reject heat to the low temperature reservoir while drawing heat from the higher temperature reservoir and this also implies that two heat reservoirs are an essential minimum for a heat engine. Thus a heat engine that draws heat continuously from a single reservoir and converts it into work as shown in Fig. 1.38, violates the Second Law of Thermodynamics.

Such a machine could derive work from the energy heat at no cost. Therefore, such a machine is called Perpetual Motion Machine of the Second Kind. Thus the Second Law of Thermodynamics may also be stated thus :

"Perpetual Motion Machine of the Second Kind is not possible to construct."

(*iii*) **Clausius Statement of Second Law of Thermodynamics or Corollary 1 of the Second Law.** *"It is impossible for the heat energy to flow spontaneously from a body at lower temperature to a body at higher temperature."* Spontaneously means without any change in surroundings. Or, it is not possible to have a system operating cyclically and passing on heat from a body at lower temperature to a body at higher temperature without doing work on the system by the surroundings.

Let us assume that system operates cyclically as heat pump and transfers heat from lower temperature body to higher temperature body without any work transfer in the system from the surrounding, as shown in Fig. 1.39 (*a*). Again let us have a heat engine which does not violate the law as shown in Fig. 1.39 (*b*). Let both of these systems, *i.e.* heat pump and heat engine be coupled. The resulting heat transfers are shown in Fig. 1.39 (*c*). This device leads to

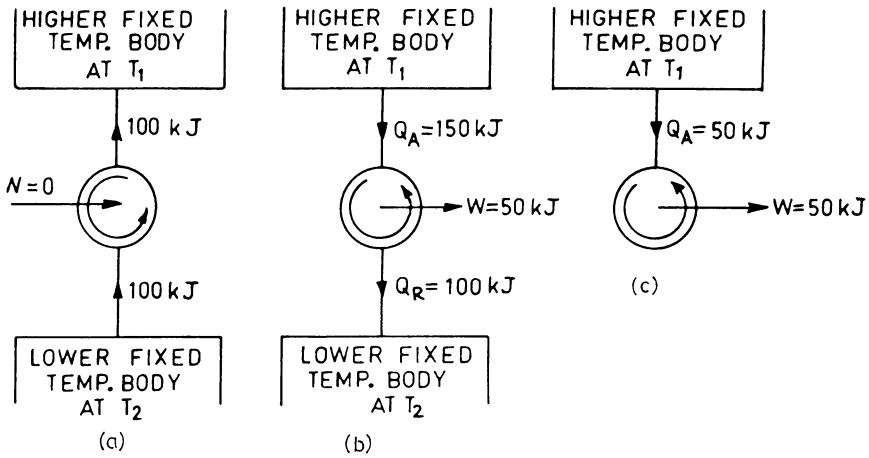


Fig. 1.39

the Perpetual Motion Machine of Second Kind and thus impossible. Thus our assumption of spontaneous transfer of heat from lower temperature body to higher temperature body is proved wrong.

The refrigeration machine will lower the temperature to a level below that of the surroundings or maintain the temperature at a level below the surroundings. Thus by work input to the machine, it is possible to draw heat from lower temperature body at T_2 and reject to higher temperature reservoir at T_1 which may be the surroundings. This is explained diagrammatically in Fig. 1.40.

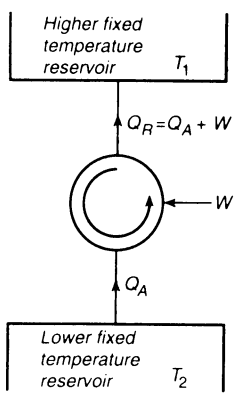


Fig. 1.40

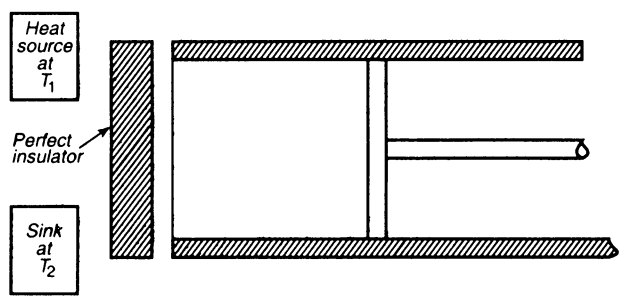


Fig. 1.41

(*iv*) **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 consists of two isothermal processes and two reversible adiabatic processes. The proposed reversible engine works as follows (Fig. 1.41). 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 large reservoir such that transfers 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. That heat source of temperature T_1 is put in contact with the 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. 1.42 representing the p-v diagram of the process. The external work is done by the system represented by $\int_{v_1}^{v_2} p\,d\,v$ for unit mass and the law of 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 $\int_{v_2}^{v_3} p\,d\,v$ 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 make it a perfect conductor. The gas is now compressed isothermally from state point (3) to state point (4).

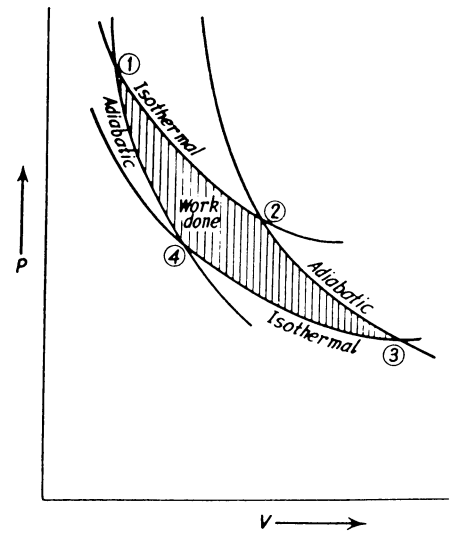


Fig. 1.42

During this process, work is done on the system given by $\int_{v_3}^{v_4} p\,d\,v$ and a corresponding heat q_R is rejected from the system at temperature T_2. Again 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 $$\oint \delta q = \oint p\,d\,v$$

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

And thermal efficiency is given by

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

$$= \frac{w}{q_A} = \frac{q_A - q_R}{q_A} \qquad \text{...(1.87)}$$

Carnot cycle is represented as 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.

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. (Consider perfect gas).

Process 1-2. $pv = C_1 \quad \Delta u = 0$

$$_1q_2 = {}_1w_2 = \int_1^2 p\,d\,v = RT_1 \log_e \frac{p_1}{p_2}$$

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

$${}_2w_3 = (u_2 - u_3) = +\,C_v\,(T_2 - T_3).$$

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

$${}_3q_4 = {}_3w_4 = -\,RT_3 \log_e \frac{p_4}{p_3}$$

Process 4-1. $pv^{\gamma} = C,\ \ {}_4q_1 = 0$

$${}_4w_1 = -\,(u_1 - u_4) = -\,C_v\,(T_1 - T_4)$$

Net work done per kg working substance

$$\oint \delta w = \oint \delta q$$

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

Since 2-3 and 4-1 are reversible adiabatics

$$\frac{p_2}{p_3} = \left(\frac{T_2}{T_3}\right)^{\frac{\gamma}{\gamma-1}} \text{ and } \frac{p_1}{p_4} = \left(\frac{T_1}{T_4}\right)^{\frac{\gamma}{\gamma-1}}$$

But $\quad T_2 = T_1$ and $T_3 = T_4$.

Therefore, $\quad \dfrac{p_2}{p_3} = \dfrac{p_1}{p_4}$ or $\dfrac{p_1}{p_2} = \dfrac{p_4}{p_3}$.

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 $\quad {}_1q_2 = RT_1 \log_e \dfrac{p_1}{p_2}$

$$\therefore \quad \eta_{th} = \frac{R\,(T_1 - T_3) \log_e p_1/p_2}{RT_1 \log_e p_1/p_2} \qquad \text{...(1.88)}$$

$$= \frac{T_1 - T_3}{T_1} \qquad \text{...(1.89)}$$

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

It may be noted that work of adiabatic compression is numerically equal to work of adiabatic expansion or

$$C_v\,(T_2 - T_3) - C_v\,(T_1 - T_4) = 0.$$

The analysis will apply to steady flow processes also giving same expression for thermal efficiency.

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

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

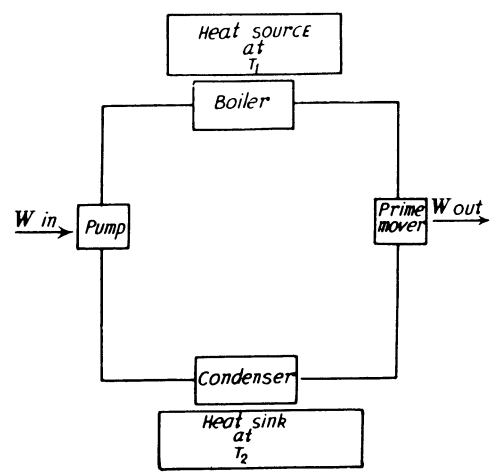


Fig. 1.43

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, $$\oint \frac{\delta q}{T} = 0 \qquad ...(1.90)$$

1.36. Further Classification of Carnot cycle

The arrangement described in Art. 1.31 is classical presentation Carnot cycle. This cycle can be described with various substances and in various ways. Steady flow cycle of a steam power plant shown in Fig. 1.43 is also an arrangement representing Carnot Cycle.

The cycle of operations is performed in different units having a defined function. The substance, *i.e.* fluid, flows from one unit to the other unit in a steady flow. The isothermal processes or heat transfers occur in boiler at T_1 and condenser at T_2. In these operations the fluid is undergoing change in phase. In the boiler, water is transferred into steam at temperature T_1 and in the reversible adiabatic expansion operation takes place in the prime mover and reversible adiabatic compression operation takes place in the pump. Thus for such a power plant also the Carnot efficiency is given by

$$\eta \text{ (Carnot)} = \frac{T_1 - T_2}{T_1} \qquad ...(1.91)$$

Further detailed discussion on Carnot cycle is given in a separate Chapter under **"Reversed Carnot Cycle"**.

1.37. Carnot Theorem or Corollary 2

No engine working between two temperatures can be more efficient than the reversible engine working between the same temperatures or the Carnot engine (hypothetical), among all engines operating between two fixed temperatures, is the most efficient.

Refer Figs. 1.44 and 1.45. This theorem is proved by *reductio absurdum.* Let engine I which is irreversible be more efficient than engine R which is reversible. Both are working between the same temperature limits of source at T_1 and sink at T_2. The heat applied to the two engine will be the same. Let it be denoted by Q_1 (let us say 100 kJ). Since irreversible engine is assumed more efficient, work done by it denoted by W_1 (let us say 60 kJ) will be more

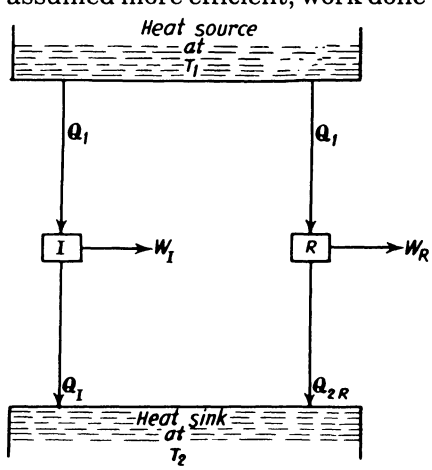


Fig. 1.44

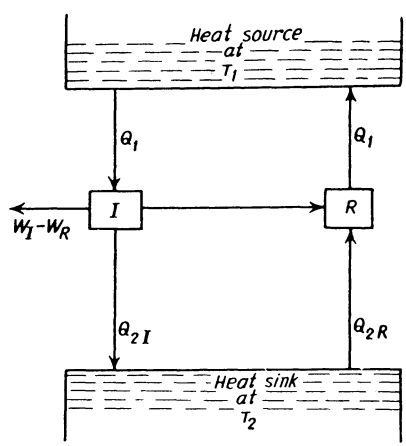


Fig. 1.45

than the work done by the reversible engine denoted by W_R (let us say 40 kcal). Now let us reverse the reversible engine and couple it to the irreversible engine, as shown in Fig. 1.45. Since R is a reversible engine, its quantities of heat and work remain unchanged except for direction. This leads to the conclusion that the irreversible engine, besides being able to drive the reversible engine, gives an additional network $W_I - W_R = W_{net}$ (*i.e.* 60 – 40 = 20 kJ) as shown in Fig. 1.45. Also the heat rejected Q_{2R} (100 – 40 = 60 kJ) by the assumed less efficient reversible engine will be more than that rejected Q_{2I} (100 – 60) = 40 kJ by the irreversible engine.

Thus for a system comprising heat source at T_1 and engines I and R, the quantity of heat ($Q_{2R} - Q_{2I}$), *i.e.* (60 – 40 = 20 kJ) is drawn from the sink and produces network ($W_1 - W_R$), (60 – 40 = 20 kJ). The energy balance of source remains. This leads to the violation of Kelvin-Planck statement of the Second Law of Thermodynamics.

If heat equivalent of $W_1 - W_R$ (60 – 40 = 20 kJ) is fed to the source at temperature T_1, we find that heat ($Q_R - Q_I$ = 20 kJ) is transferred from low temperature sink at T_2 to high temperature source at T_I without doing any external work on the system. This violates Clausius' statement of the Second Law of Thermodynamics.

Thus the assumption that I is more efficient than R is not true. This proves the Carnot theorem. This may lead to enunciation of another statement as Corollary 3.

All reversible engines working between two fixed temperatures have the same efficiency.

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 of heat 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. 1.46, we note that heat enters the system at the boiler and leaves at the condenser. The difference between these equals work at the turbine and pump *i.e.*

$$(Q_A - Q_R) = (W_s - W) \qquad ...(1.92)$$

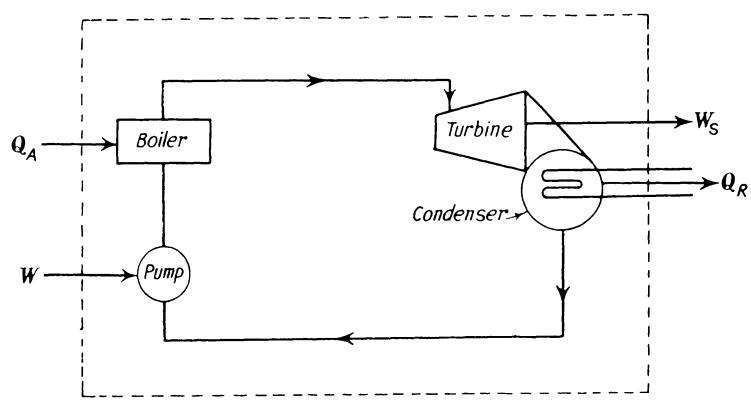


Fig. 1.46

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 to condenser where it changes 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

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

$$\eta_{th} = \frac{W_{turbine} - W_{pump}}{Q_A} = \frac{Q_A - Q_R}{Q_A} \quad ...(1.93)$$

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

1.40. Thermal Efficiency of Heat Pump or Coefficient of Performancy of Heat Pump

Efficiency of a device is defined according to an objective in mind. If the objective is to transfer heat Q_R to a high temperature body, *i.e.* to pump heat such as to heat the houses in the winter season, the efficiency may be written down as

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

But in case of such system, the term efficiency is replaced by another term. Coefficient of Performance denoted by *COP* to avoid confusion between heat engine and heat pump. Thus

$$COP_{(Heat\ pump)} = \frac{Q_R}{Q_R - Q_A} \quad ...(1.94)$$

But if the objective in mind is the abstraction of heat *i.e.* to pump out heat such as to cool the houses in summer season, the device is called refrigerator and coefficient of performance is given as :

$$COP_{Refrigerator} = \frac{Q_A}{Q_R - Q_A} \quad ...(1.95)$$

The objective in case of heat engine is illustrated in Fig. 1.47. Heat is drawn in from high temperature source and amount Q_A is fed to the heat engine. Network $(_{Net})$ is obtained from the heat engine and the amount of heat Q_R is rejected to the low temperature heat sink. Thus heat flows from high temperature heat source to low temperature heat sink *via* the heat engine, where only part of the heat from the heat source gets converted to work and delivered as output. Thus the objective to be more efficiently achieved will depend upon how large the portion of Q_A is converted to output work.

The objective in case of Heat Pump is illustrated in Fig. 1.48.

We have $$\oint \delta Q = Q_R - Q_A = \oint \delta W = W_S$$

Work is done on the system and heat is transferred from low temperature source to high temperature sink by supplying energy by way of work from the surrounding to the system.

Thus, if the energy sought is Q_R, *i.e.* heating or the system is treated as a heat pump, we have

$$COP = \frac{Q_R}{q_R - Q_A} = \frac{Q_R}{W_S} \quad ...(1.96)$$

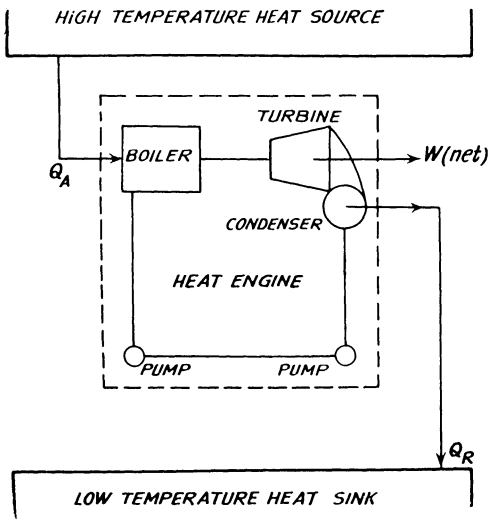


Fig. 1.47

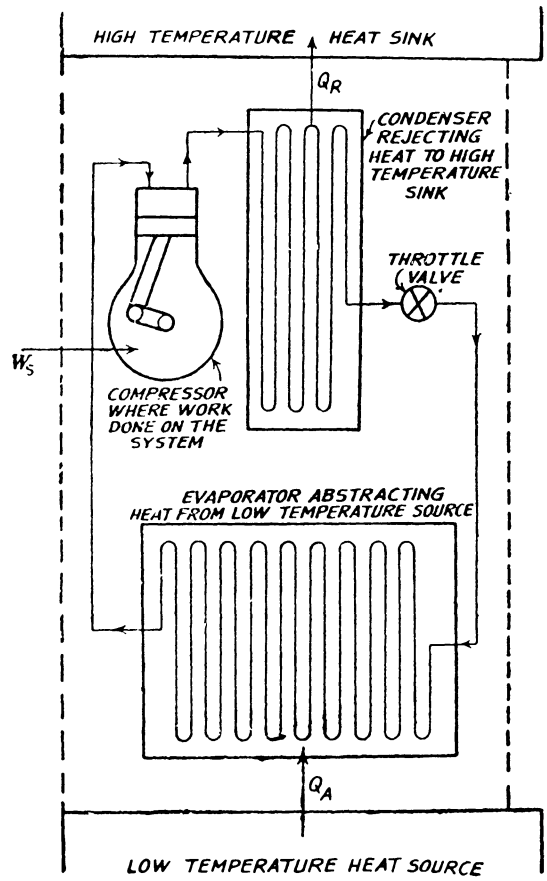


Fig. 1.48

If the energy sought is Q_A *i.e.*, abstraction of heat or refrigeration or the system is a refrigerator.

$$COP = \frac{Q_A}{q_R - Q_A} = \frac{Q_A}{W_S} \qquad ...(1.97)$$

1.41. Entropy

There exists a property called Entropy of the system such that for any reversible process from state point 1 to state point 2 its change is given by

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{rev.}$$

1.42. Entropy Changes During Processes

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

or

$$\Delta S = \int \left(\frac{dU + \delta W}{T}\right)_{rev.} \qquad ...(1.98)$$

or

$$\Delta S = \int \left(\frac{dU + pdV}{T}\right)_{rev.} \qquad ...(1.99)$$

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

$$dS = \frac{dU + pdV}{T} \quad ...(1.100)$$

or

$$TdS = dU + pdV \quad ...(1.101)$$

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

$$TdS = dU + pdV = d\,(H - pV) + pdV$$
$$= dH - pdV - Vdp + pdV = dH - Vdp$$

i.e.

$$TdS = dH - Vdp \quad ...(1.102)$$

For unit mass

$$(s_2 - s_1) = C_v \log_e \frac{T_2}{T_1} \text{ for constant volume process} \quad ...(1.103)$$

$$= C_p \log_e \frac{T_2}{T_1} \text{ for constant volume process} \quad ...(1.104)$$

$$= R \log_e \frac{v_2}{v_1} \text{ for isothermal process} \quad ...(1.105)$$

$$= -R \log_e \frac{p_2}{p_1} \text{ for isothermal process} \quad ...(1.106)$$

$$= \frac{(\gamma - n)\,R}{\gamma - 1} \log_e \frac{v_2}{v_1} \text{ for polytropic process} \quad ...(1.107)$$

$$= C_v \left(\frac{\gamma - n}{1 - n} \right) \log_e \frac{T_2}{T_1} \text{ for polytropic process} \quad ...(1.108)$$

1.43. Temperature-Entropy Diagram

We have

$$_1Q_2 = \int_{s_1}^{s_2} . \, TdS$$

This integral can be represented graphically as the area under the curve drawn on temperature-entropy co-ordinates in the same way as $_1W_2 = \int_{V_1}^{V_2} dV$ is represented on pressure-volume co-ordinates, as shown in Figs. 1.49 and 1.50.

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 d one in a cycle, and the area enclosed in the cycle of processes on T-s co-ordinates represents heat transfer, provided course that all the processes of the cycle are reversible. And by First Law of Thermodynamics

$$\oint \delta Q = \oint \delta W$$

or heat transfer to the system during cycle

= Work done by the system during cycle.

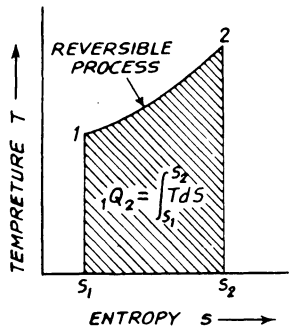


Fig. 1.49

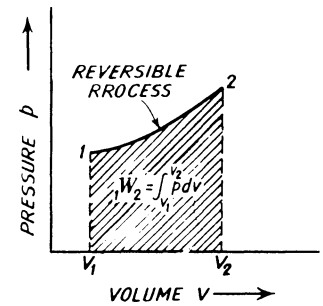


Fig. 1.50

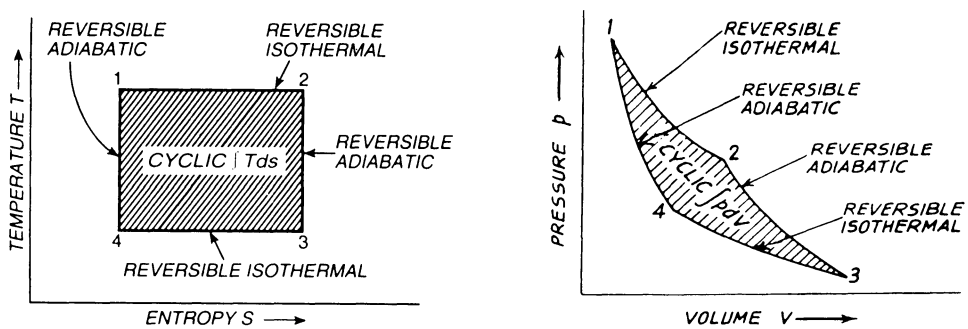


Fig. 1.51

This leads to a very important conclusion that the enclosed area for a cycle of processes (reversible) represents work on both p-V as well as T-s co-ordinates. Thus, if cycle comprising two isothermal processes and two isentropic processes is represented on T-s and p-V co-ordinates as shown in Fig. 1.51 (a) and (b), the hatched area represents work done. This is Carnot cycle discussed later in details.

Problem. *An inventor 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°C 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

$$\eta_{carnot} = \frac{T_1 - T_2}{T_1} = \frac{(727 + 273) - (273 + 27)}{(727 + 273)}$$

$$= \frac{1000 - 300}{1000} = 0.7 \text{ or } 70\%$$

The actual thermal efficiency claimed

$$\eta_{actual} = \frac{\text{Work}}{\text{Heat supplied}} = \frac{760 \times 1000 \times 60 \times 60}{4 \times 75{,}000 \times 1000}$$

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

TEST YOUR COMPREHENSION

(Tick Mark Correct Statements)

1. Thermodynamics system may be defined as quantity of matter upon which attention is focused for study if

(*a*) it is only bounded by real surfaces

(*b*) it is not bounded by imaginary surfaces

(*c*) the boundary surfaces are constant in shape and volume

(*d*) it is bounded by either real surfaces or imaginary surfaces irrespective of shape or volume.

2. Universe is defined as :

(*a*) Isolated system un-influenced by surroundings is called Universe

(*b*) System and surroundings combined constitute Universe whether these interact with each other or not

(*c*) System which only interacts with surroundings is part of the universe

(*d*) System and surroundings put together form universe only if there is interaction between them.

3. A centrifugal fan forms

(*a*) closed system (*b*) open system (*c*) isolated system (*d*) none of the above.

4. Zeroth Law of Thermodynamics defines

(*a*) internal energy (*b*) enthalpy (*c*) temperature (*d*) pressure.

5. 1 mm H_2O is equal to

(*a*) 100×10^{-6} bar (*b*) 0.00001 kgf/cm^2 (*c*) 98.0665 N/m^2 (*d*) 0.075 mm Hg.

6. – 40°C is equal to

(*a*) –40°F (*b*) 230°K (*c*) 400°R (*d*) – 72°F.

7. For constant volume process on a gas the value of index n for the path followed is equal to

(*a*) 1 (*b*) zero (*c*) $\propto$ (*d*) 1.4.

8. A gas expands from initial pressure p_1 and volume V_1 to final volume $5V_1$. The work obtained is maximum when n is

(*a*) 1.4 (*b*) 1 (*c*) zero (*d*) $\propto$.

9. Air expands from initial pressure p_1 and volume V_1 to final volume $5V_1$ following the law $pV^n = C$

(*a*) greater the value of n, greater the work obtained

(*b*) smaller the value of n, greater the work obtained

(*c*) for $n = 0$ the work obtained is the greatest

(*d*) for $n = 1.4$ the work obtained is the greatest.

10. Universal Gas Constant of a perfect gas

(*a*) increases with temperature (*b*) decreases with temperature

(*c*) increases with increase in molecular weight (*d*) is always constant.

11. Which of the following can be used as properties of a system

(*a*) $\int \frac{dT}{T} - \frac{vdp}{T}$ (*b*) $\int \frac{dT}{T} + \frac{pdv}{v}$ (*c*) $\int pdv$ (*d*) $\int vdp$.

12. Characteristic gas constant of any perfect gas

(*a*) increases with increase in temperature (*b*) increase with increase in pressure

(*c*) is a function of pressure and temperature (*d*) is constant.

13. The ratio of specific heats of a gas at constant pressure and at constant volume is

(*a*) always constant (*b*) always varies with pressure

(*c*) always varies with temperature (*d*) none of the above.

14. Characteristic equation of gas is given by

(*a*) $pv = RT$ when v = specific volume (*b*) $pv = mRT$, where m = mass of gas

(*c*) $pv^n = C$ (*d*) $pv^\gamma = C$.

ANSWERS

1. (*d*)	**2.** (*b*)	**3.** (*b*)	**4.** (*c*)	**5.** (*b*)
6. (*a*)	**7.** (*c*)	**8.** (*c*)	**9.** (*c*)	**10.** (*d*)
11. (*a*)	**12.** (*d*)	**13.** (*c*)	**14.** (*a*).	

TEST QUESTIONS

1. Classify each of the following systems whether it is an open or closed system :

(*a*) Air compressor (*b*) Carburettor

(*c*) Pressure cooker (*d*) Radiator of an automobile

(*e*) Teak kettle.

2. What do you understand by Intensive and Extensive properties ? Classify the following properties with their units in metric system :

(*a*) Specific weight (*b*) Volume

(*c*) Specific volume (*d*) Density

(*e*) Molecular weight (*f*) Pressure

(*g*) Temperature (*h*) Velocity.

3. State the Zeroth Law of Thermodynamics. How is mercury in thermometer able to find the temperature of a body using the Zeroth Law of Thermodynamics.

4. Distinguish between absolute pressure and gauge pressure. How is one related to the other in case of vacuum.

5. Explain Boyles Law and Charles law as applied to perfect gas. Which of these laws can be used to evaluate Absolute Zero temperature and how ?

PROBLEMS FOR PRACTICE (NUMERICALS)

1. A piston has an area of 5 cm^2. What mass must the piston have if it exerts a pressure of 50 kPa above atmospheric pressure on the gas enclosed in the cylinder.

2. A pressure gauge reads 2.4 bar and the barometer read 75 cm of Hg. Calculate the absolute pressure in bar and in the standard atmospheres.

3. A manometer has a liquid of density 800 kg/m^3, the difference in level of the two legs in 300 mm. Determine the pressure difference read by it in kPa.

4. A vertical composite liquid column with its upper end exposed to atmosphere of 45 cm of Hg (specific gravity of Hg is 13.5951), 65 cm of water (specific gravity of water is 1) and 80 cm of oil (specific gravity of oil is 0.8). Determine the pressure

(*i*) at the bottom of the column

(*ii*) at the inter-surface of oil and water

(*iii*) at the inter-surface of water and mercury.

5. A manometer containing water and mercury connects two pressure region X and Y as shown in Fig. P.1.1. If P = 4 bar gauge, find p_x.

6. The air supply to an internal combustion engine is metered by observing the pressure drop across an orifice in the air supply line to the engine, the pressure drop is measured by means of a manometer containing paraffin having a specific gravity of 0.81. Express a difference of level of 25 cm in the manometer in

(*a*) kgf/cm^2. (*b*) metres of air.

(*c*) kPa. (*d*) mm H_2O.

(*e*) mm Hg. (*f*) bar.

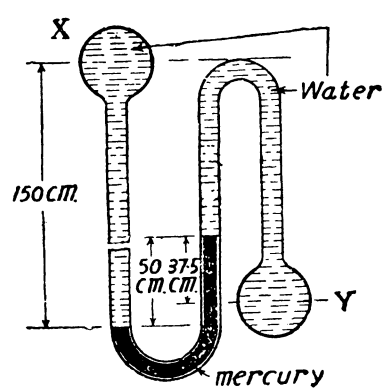


Fig. P-1.1

7. Define a new temperature scale, say °B in which the boiling and the freezing points of water are 500 °B and 100°B respectively.
   (*a*) Co-relate this scale with centigrade scale.
   (*b*) °B reading on the scale is some number on corresponding absolute temperature scale. What is this absolute temperature on °B.
8. Define quasi-static process and drive an expression for the work done. Explain its limitations giving examples.
9. 0.084 m^3 of a gas is expanded in a cylinder which causes the pressure to fall from 7 to 2.45 bar. If the expansion of follows the law $pV^{1.1} = C$, find final volume of the gas.
10. A non-flow reversible process occurs for which $p = 3V^2 + 1/V$, where p is in bar and V in m^3. What is the work done when V changes from 0.5 to 0.1 m^3 ?
11. Determine the work done by 1 kg fluid system as it expands slowly within the frictionless piston cylinder arrangement from an initial pressure and volume of 5 bar to a final volume of 0.8 m^3 in accordance with the following defining arrangement :
    (*a*) $p = C$ (*b*) $pV = C$
    (*c*) $pv^{1.4} = C$ (*d*) $pV^2 = C$.
12. Write short notes on :
    (*a*) System (*b*) Properties
    (*c*) Path function and point function
    (*d*) Zeroth law of thermodynamics
    (*e*) Work and heat.
13. During a particular process, the specific heat capacity of the system is given by $C = 0.3 + 0.002\,T$. Find the heat transferred and mean specific heat of the gas of 0.2 kg from 27 °C to 127°C.
14. Air at pressure of 1 bar gauge expands to three times its volume, the temperature being constant. Determine the absolute pressure at the end of expansion if the barometer reads 550 mm Hg.
15. Find the specific weight of nitrogen at 15°C and pressure of 1 bar and also the value of its gas constant R. Molecular weight of nitrogen is 28.02.
16. Calculate the mass of oxygen in a cylinder with a capacity of 100 litres at a temperature of 20°C. The pressure in the cylinder is maintained at 80 bar.
17. 5 cubic metres of air at 0°C and a pressure of 3 bar is heated to 80°C. Determine (*i*) change of internal energy, (*ii*) heat supplied, (*iii*) mechanical work done. $\gamma = 14$.
18. 0.56 cubic metres of gas of a pressure of 2.95 bar and temperature of 30°C is compressed to 20.6 bar. The rise in temperature is 370°C. Determine its final volume. Calculate also the mass of the gas if it is nitrogen with $R = 296.87$ J/kg °K.
19. A cylinder contains 3.14 kg of oxygen at 4.90 bar and temperature of 27°C. Determine the internal volume of the cylinder and its capacity to contain this mass at one physical atmosphere and 20°C. Assume $R = 259.8$ J/kg °K.
20. Determine the volume of 6 kg air at a pressure of 3.925 bar and temperature of 50°C if C_v for air is 0.71 kJ/kg °K and C_p is 1.0 kJ/kg °K.