

1

Basic Concepts of Thermodynamics

-
- 1.1. Definition of thermodynamics. 1.2. Thermodynamic systems—System, boundary and surroundings—Closed system—Open system—Isolated system—Adiabatic system—Homogeneous system—Heterogeneous system. 1.3. Macroscopic and microscopic points of view. 1.4. Pure substance. 1.5. Thermodynamic equilibrium. 1.6. Properties of systems. 1.7. State. 1.8. Process. 1.9. Cycle. 1.10. Point function. 1.11. Path function. 1.12. Temperature. 1.13. Zeroth law of thermodynamics. 1.14. The thermometer and thermometric property—Introduction—Measurement of temperature—The international practical temperature scale—Ideal gas. 1.15. Pressure—Definition of pressure—Unit for pressure—Types of pressure measurement devices—Mechanical-type instruments—Important types of pressure gauges. 1.16. Specific volume. 1.17. Reversible and irreversible processes. 1.18. Energy, work and heat—Energy—Work and heat. 1.19. Reversible work—Highlights—Objective type questions—Theoretical questions—Unsolved examples.
-

1.1. DEFINITION OF THERMODYNAMICS

Thermodynamics may be defined as follows :

Thermodynamics is an axiomatic science which deals with the relations among heat, work and properties of system which are in equilibrium. It describes state and changes in state of physical systems.

Or

Thermodynamics is the science of the regularities governing processes of energy conversion.

Or

Thermodynamics is the science that deals with the interaction between energy and material systems.

Thermodynamics, basically entails four laws or axioms known as Zeroth, First, Second and Third law of thermodynamics.

- the First law throws light on concept of internal energy.
- the Zeroth law deals with thermal equilibrium and establishes a concept of temperature.
- the Second law indicates the limit of converting heat into work and introduces the principle of increase of entropy.
- third law defines the absolute zero of entropy.

These laws are based on experimental observations and have no mathematical proof. Like all physical laws, these laws are based on logical reasoning.

1.2. THERMODYNAMIC SYSTEMS

1.2.1. System, Boundary and Surroundings

System. A system is a finite quantity of matter or a prescribed region of space (Refer Fig. 1.1)

Boundary. The actual or hypothetical envelope enclosing the system is the boundary of the system. The boundary may be fixed or it may move, as and when a system containing a gas is

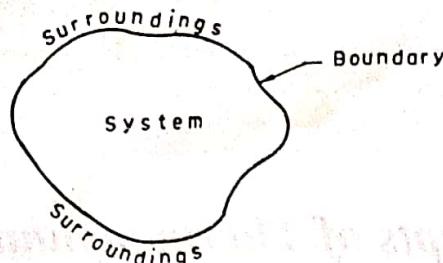


Fig. 1.1. The system.

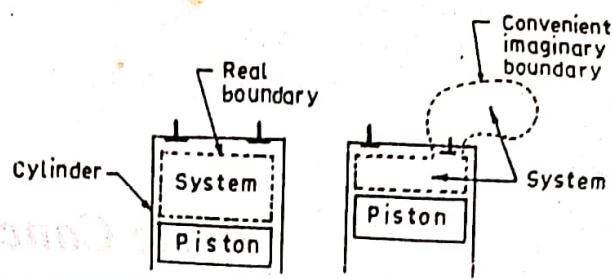


Fig. 1.2. The real and imaginary boundaries.

compressed or expanded. The boundary may be *real* or *imaginary*. It is not difficult to envisage a real boundary but an example of imaginary boundary would be one drawn around a system consisting of the fresh mixture about to enter the cylinder of an I.C. engine together with the remanants of the last cylinder charge after the exhaust process (Refer Fig. 1.2).

1.2.2. Closed System

Refer Fig. 1.3. If the boundary of the system is impervious to the flow of matter, it is called a *closed system*. An example of this system is mass of gas or vapour contained in an engine cylinder, the boundary of which is drawn by the cylinder walls, the cylinder head and piston crown. Here the *boundary is continuous and no matter may enter or leave*.

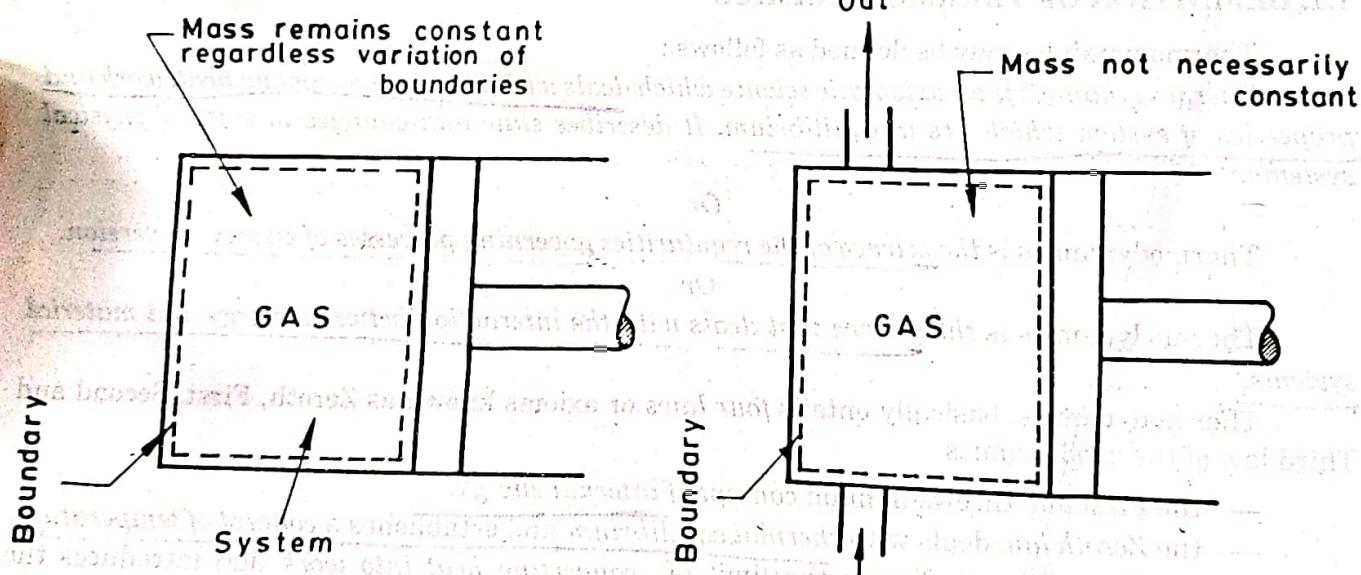


Fig. 1.3. Closed system.

1.2.3. Open System

Refer Fig. 1.4. An open system is one in which *matter flows into or out of the system*. Most of the engineering systems are open.

1.2.4. Isolated System

An isolated system is that system which *exchanges neither energy nor matter with any other system or with environment*.

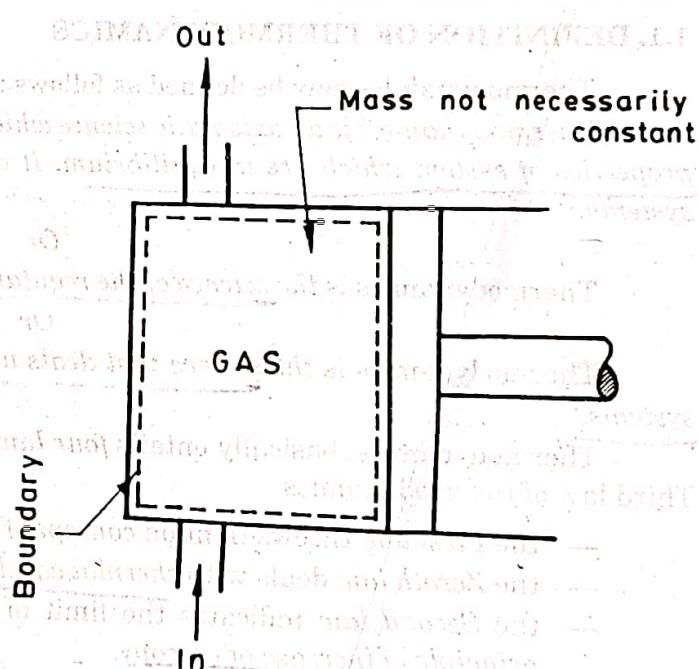


Fig. 1.4. Open system.

BASIC CONCEPTS OF THERMODYNAMICS

1.2.5. Adiabatic System

An adiabatic system is one which is thermally insulated from its surroundings. It can, however, exchange work with its surroundings. If it does not, it becomes an isolated system.

Phase. A phase is a quantity of matter which is homogeneous throughout in chemical composition and physical structure.

1.2.6. Homogeneous System

A system which consists of a single phase is termed as homogeneous system. Examples :

Mixture of air and water vapour, water plus nitric acid and octane plus heptane.

1.2.7. Heterogeneous System

A system which consists of two or more phases is called a heterogeneous system. Examples :

Water plus steam, ice plus water and water plus oil.

1.3. MACROSCOPIC AND MICROSCOPIC POINTS OF VIEW

Thermodynamic studies are undertaken by the following two different approaches.

1. Macroscopic approach—(*Macro mean big or total*)

2. Microscopic approach—(*Micro means small*)

These approaches are discussed (in a comparative way) below :

S. No.	Macroscopic approach	Microscopic approach
1.	In this approach a certain quantity of matter is considered <u>without taking into account the events occurring at molecular level</u> . In other words this approach to thermodynamics is concerned with <u>gross or overall behaviour</u> . This is known as <u>classical thermodynamics</u> .	The approach considers that the system is made up of a very large number of discrete particles known as <u>molecules</u> . These molecules have different velocities and energies. The values of these energies are constantly changing with time. This approach to thermodynamics which is concerned directly with <u>the structure of the matter</u> is known as <u>statistical thermodynamics</u> .
2.	The analysis of macroscopic system requires <u>simple mathematical formulae</u> .	The behaviour of the system is found by using statistical methods as the number of molecules is very large. So advanced statistical and mathematical methods are needed to explain the changes in the system.
3.	The values of the properties of the system are their <u>average values</u> . For example, consider a sample of a gas in a closed container. The <u>pressure</u> of the gas is the average value of the pressure exerted by millions of individual molecules. Similarly the <u>temperature</u> of this gas is the average value of translational kinetic energies of millions of individual molecules. These properties like <u>pressure</u> and <u>temperature</u> can be measured very easily. The changes in properties can be felt by our senses.	The properties like <u>velocity</u> , <u>momentum</u> , <u>impulse</u> , <u>kinetic energy</u> , <u>force of impact</u> etc. which describe the molecule <u>cannot be easily measured by instruments</u> . Our senses cannot feel them.
4.	In order to describe a system only a few properties are needed.	Large number of variables are needed to describe a system. So the approach is complicated.

Note. Although the macroscopic approach seems to be different from microscopic one, there exists a relation between them. Hence when both the methods are applied to a particular system, they give the same result.

1.4. PURE SUBSTANCE

A pure substance is one that has a homogeneous and invariable chemical composition even though there is a change of phase. In other words, it is a system which is (a) homogeneous in composition, (b) homogeneous in chemical aggregation. Examples : Liquid, water, mixture of liquid water and steam, mixture of ice and water. The mixture of liquid air and gaseous air is not a pure substance.

1.5. THERMODYNAMIC EQUILIBRIUM

A system is in *thermodynamic equilibrium* if the temperature and pressure at all points are same ; there should be no velocity gradient ; the chemical equilibrium is also necessary. Systems under temperature and pressure equilibrium but not under chemical equilibrium are sometimes said to be in metastable equilibrium conditions. It is only under thermodynamic equilibrium conditions that the properties of a system can be fixed.

Thus for attaining a state of *thermodynamic equilibrium* the following three types of equilibrium states must be achieved :

1. **Thermal equilibrium.** The temperature of the system does not change with time and has same value at all points of the system.

2. **Mechanical equilibrium.** There are no unbalanced forces within the system or between the surroundings. The pressure in the system is same at all points and does not change with respect to time.

3. **Chemical equilibrium.** No chemical reaction takes place in the system and the chemical composition which is same throughout the system does not vary with time.

1.6. PROPERTIES OF SYSTEMS

A property of a system is a characteristic of the system which depends upon its state, but not upon how the state is reached. There are two sorts of property :

1. **Intensive properties.** These properties do not depend on the mass of the system. Examples : Temperature and pressure.

2. **Extensive properties.** These properties depend on the mass of the system. Example : Volume. Extensive properties are often divided by mass associated with them to obtain the intensive properties. For example, if the volume of a system of mass m is V , then the specific volume of matter within the system is $\frac{V}{m} = v$ which is an intensive property.

1.7. STATE

State is the condition of the system at an instant of time as described or measured by its properties. Or each unique condition of a system is called a state.

It follows from the definition of state that each property has a single value at each state. Stated differently, all properties are *state or point functions*. Therefore, all properties are identical for identical states.

On the basis of the above discussion, we can determine if a given variable is *property* or not by applying the following tests :

- A variable is a property, if and only if, it has a single value at each equilibrium state.
- A variable is a property, if and only if, the change in its value between any two prescribed equilibrium states is single-valued.

Therefore, any variable whose change is fixed by the end states is a property.

(Learn)

BASIC CONCEPTS OF THERMODYNAMICS

1.8. PROCESS

A process occurs when the system undergoes a change in a state or an energy transfer at a steady state. A process may be non-flow in which a fixed mass within the defined boundary is undergoing a change of state. Example : a substance which is being heated in a closed cylinder undergoes a non-flow process (Fig. 1.3). Closed systems undergo non-flow processes. A process may be a flow process in which mass is entering and leaving through the boundary of an open system. In a steady flow process (Fig. 1.4) mass is crossing the boundary from surroundings at entry, and an equal mass is crossing the boundary at the exit so that the total mass of the system remains constant. In an open system it is necessary to take account of the work delivered from the surroundings to the system at entry to cause the mass to enter, and also of the work delivered from the system at surroundings to cause the mass to leave, as well as any heat or work crossing the boundary of the system.

also known as reversible process
Quasi-static process. Quasi means 'almost'. A quasi-static process is also called a **reversible process**. This process is a succession of equilibrium states and infinite slowness is its characteristic feature.

1.9. CYCLE

Any process or series of processes whose end states are identical is termed a **cycle**. The processes through which the system has passed can be shown on a state diagram, but a complete section of the path requires in addition a statement of the heat and work crossing the boundary of the system. Fig. 1.5 shows such a cycle in which a system commencing at condition '1' changes in pressure and volume through a path 123 and returns to its initial condition '1'.

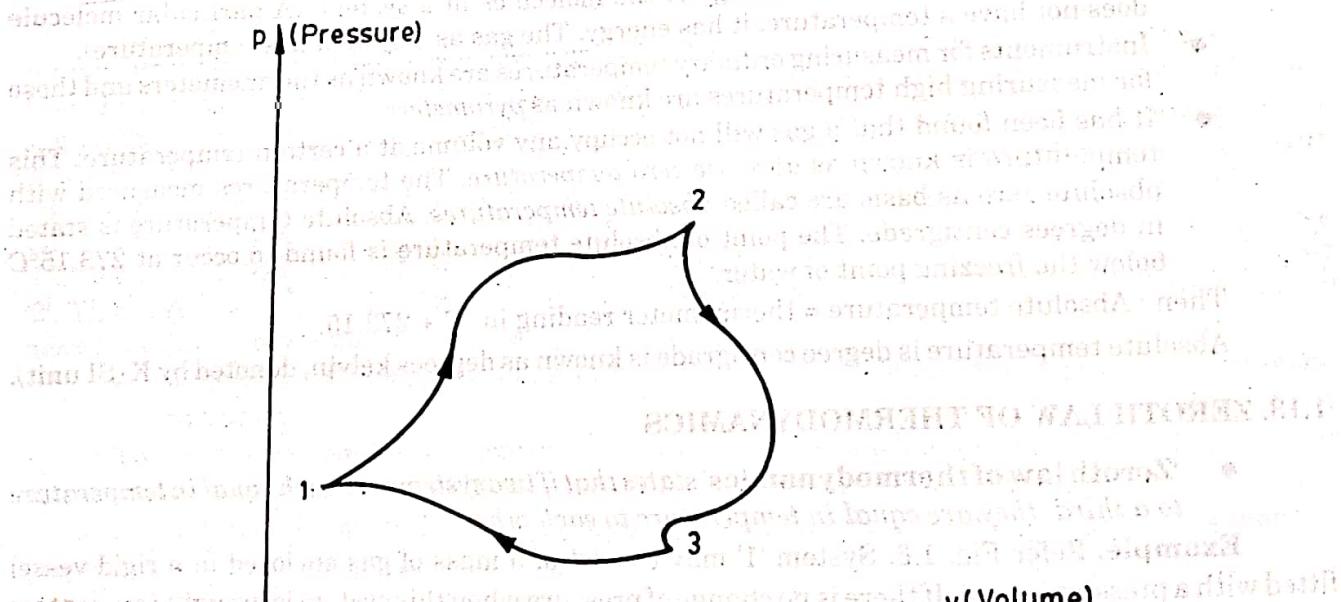


Fig. 1.5. Cycle of operations.

1.10. POINT FUNCTION

When two properties locate a **point** on the graph (co-ordinate axes) then those properties are called as **point function**.

Examples. Pressure, temperature, volume etc.

$$\int_1^2 dV = V_2 - V_1 \text{ (an exact differential).}$$

1.11. PATH FUNCTION

There are certain quantities which cannot be located on a graph by a *point* but are given by the *area* or so, on that graph. In that case, the area on the graph, pertaining to the particular process, is a function of the path of the process. Such quantities are called *path functions*.

Examples. Heat, work etc.

Heat and work are *inexact differentials*. Their change cannot be written as difference between their end states.

Thus $\int_1^2 \delta Q \neq Q_2 - Q_1$ and is shown as ${}_1Q_2$ or Q_{1-2}

Similarly $\int_1^2 \delta W \neq W_2 - W_1$, and is shown as ${}_1W_2$ or W_{1-2}

Note. The operator δ is used to denote inexact differentials and operator d is used to denote exact differentials.

1.12. TEMPERATURE

- The temperature is a thermal state of a body which distinguishes a hot body from a cold body. The temperature of a body is proportional to the stored molecular energy i.e. the average molecular kinetic energy of the molecules in a system. (A particular molecule does not have a temperature, it has energy. The gas as a system has temperature).
- Instruments for measuring ordinary temperatures are known as thermometers and those for measuring high temperatures are known as pyrometers.
- It has been found that a gas will not occupy any volume at a certain temperature. This temperature is known as absolute zero temperature. The temperatures measured with absolute zero as basis are called absolute temperatures. Absolute temperature is stated in degrees centigrade. The point of absolute temperature is found to occur at 273.15°C below the freezing point of water.

Then : Absolute temperature = thermometer reading in $^\circ\text{C}$ + 273.15.

Absolute temperature in degree centigrade is known as degrees kelvin, denoted by K (SI unit).

1.13. ZERO TH LAW OF THERMODYNAMICS

- 'Zeroth law of thermodynamics' states that if two systems are each equal in temperature to a third, they are equal in temperature to each other.

Example. Refer Fig. 1.6. System '1' may consist of a mass of gas enclosed in a rigid vessel fitted with a pressure gauge. If there is no change of pressure when this system is brought into contact with system '2' a block of iron, then the two systems are equal in temperature (assuming that the systems 1 and 2 do not react each other chemically or electrically). Experiment reveals that if system '1' is brought into contact with a third system '3' again with no change of properties then systems '2' and '3' will show no change in their properties when brought into contact provided they do not react with each other chemically or electrically. Therefore, '2' and '3' must be in equilibrium.

BASIC CONCEPTS OF THERMODYNAMICS

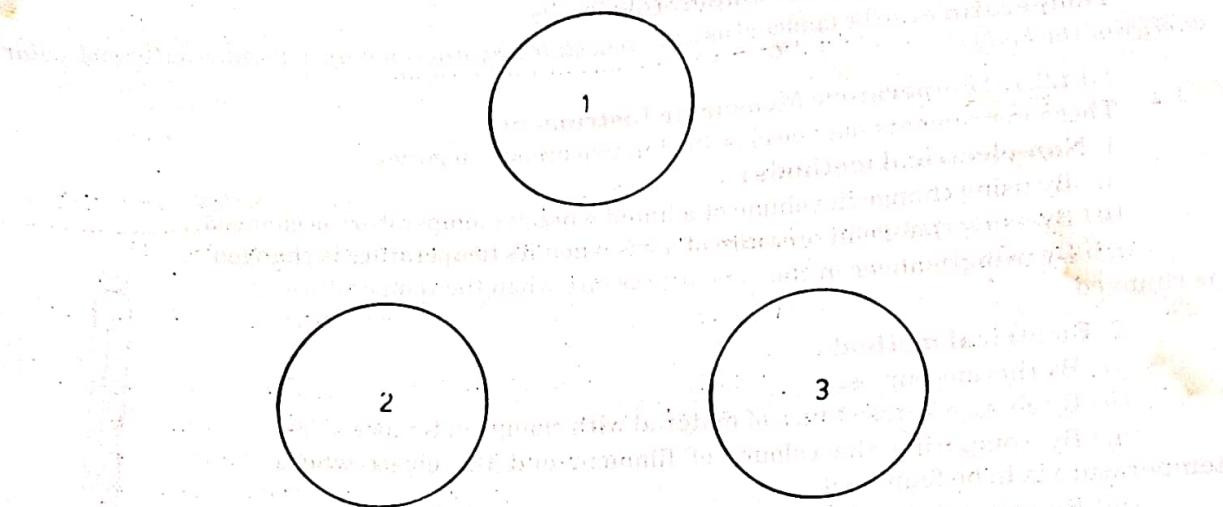


Fig. 1.6. Zeroth law of thermodynamics.

- This law was enunciated by R.H. Fowler in the year 1931. However, since the first and second laws already existed at that time, it was designated as *zeroth law* so that it *precedes* the first and second laws *to form a logical sequence*.

1.14. THE THERMOMETER AND THERMOMETRIC PROPERTY

1.14.1. Introduction

The zeroth law of thermodynamics provides the basis for the measurement of temperature. It enables us to compare temperatures of two bodies '1' and '2' with the help of a third body '3' and say that the temperature of '1' is the same as the temperature of '2' without actually bringing '1' and '2' in thermal contact. In practice, body '3' in the zeroth law is called the **thermometer**. It is brought into thermal equilibrium with a set of standard temperature of a body '2', and is thus calibrated. Later, when any other body '1' is brought in thermal communication with the thermometer, we say that the body '1' has attained equality of temperature with the thermometer, and hence with body '2'. This way, the body '1' has the temperature of body '2' given for example by, say the height of mercury column in the thermometer '3'.

- The height of mercury column in a thermometer, therefore, becomes a **thermometric property**.

There are other methods of temperature measurement which utilize various other properties of materials, those are functions of temperature, as thermometric properties.

Six different kinds of thermometers, and the names of the corresponding thermometric properties employed are given below :

Thermometer

1. Constant volumes gas
2. Constant pressure gas
3. Alcohol or mercury-in-glass
4. Electric resistance
5. Thermocouple
6. Radiation (pyrometer)

Thermometric property

- | |
|---------------------------------------|
| Pressure (p) |
| Volume (V) |
| Length (L) |
| Resistance (R) |
| Electromotive force (E) |
| Intensity of radiation (I or J) |

Solution. Equating pressure on both arms above the line XX (Fig. 1.26), we get

$$p_{\text{gas}} + p_{\text{liquid}} = p_{\text{atm.}} \quad \dots(i)$$

$$\text{Now, } p_{\text{liquid}} = \rho g h$$

$$= (0.8 \times 1000) \times 9.81 \times \frac{170}{1000}$$

$$= 1334.16 \text{ N/m}^2$$

$$= 0.0133416 \text{ bar}$$

$$p_{\text{atm.}} = 760 \text{ mm of Hg} = 1.01325 \text{ bar}$$

Substituting these values in eqn. (i) above, we have

$$p_{\text{gas}} + 0.0133416 = 1.01325$$

$$\therefore p_{\text{gas}} = 0.9999 \text{ bar. (Ans.)}$$

Example 1.9. Estimate the mass of a piston that can be supported by a gas entrapped under the piston in a 200 mm diameter vertical cylinder when a manometer indicates a difference of 117 mm of Hg column for the gas pressure. (Poona University, May 1994)

Solution. Refer Fig. 1.27.

Let m = mass of the piston, kg.

p = pressure of the gas

= 117 mm of Hg column

Dia. of vertical cylinder, $d = 200 \text{ mm}$

Now, downward force = $m.g$ $\dots(i)$

and

upward force = $p \times \pi/4 d^2$ $\dots(ii)$

Equating eqns. (i) and (ii), we get

$$m.g = p \times \pi/4 d^2$$

$$m \times 9.81 = \left(13.6 \times 1000 \times 9.81 \times \frac{117}{1000} \right) \times \frac{\pi}{4} \times \left(\frac{200}{1000} \right)^2 \quad (\because p = \rho gh)$$

$$m = 49.989 \text{ kg. (Ans.)}$$

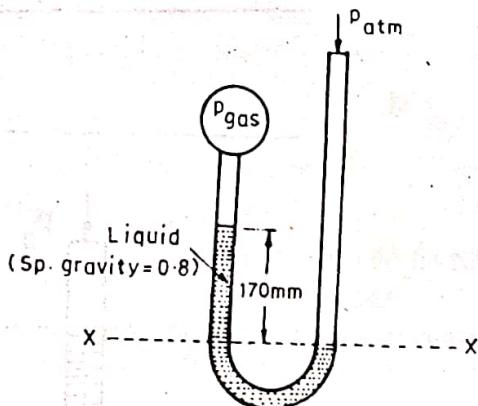


Fig. 1.26

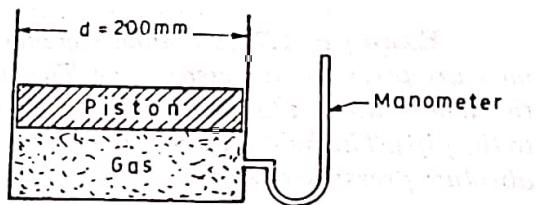


Fig. 1.27

1.17. REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible process. A reversible process (also sometimes known as quasi-static process) is one which can be stopped at any stage and reversed so that the system and surroundings are exactly restored to their initial states.

This process has the following characteristics :

✓ 1. It must pass through the same states on the reversed path as were initially visited on the forward path.

✓ 2. This process when undone will leave no history of events in the surroundings.

✓ 3. It must pass through a continuous series of equilibrium states.

No real process is truly reversible but some processes may approach reversibility, to close approximation.

Examples. Some examples of nearly reversible processes are :

(i) Frictionless relative motion.

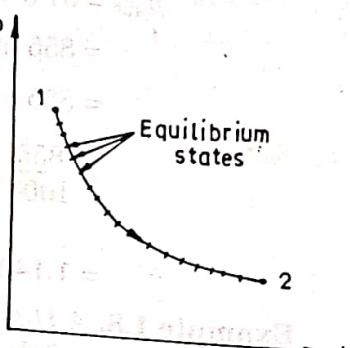


Fig. 1.28. Reversible process.

BASIC CONCEPTS OF THERMODYNAMICS

- (ii) Expansion and compression of spring.
- (iii) Frictionless adiabatic expansion or compression of fluid.
- (iv) Polytropic expansion or compression of fluid.
- (v) Isothermal expansion or compression.
- (vi) Electrolysis.

Irreversible process. An irreversible process is one in which heat is transferred through a finite temperature.

Examples.

- | | |
|-----------------------------------|--|
| (i) Relative motion with friction | (ii) Combustion |
| (iii) Diffusion | (iv) Free expansion |
| (v) Throttling | (vi) Electricity flow through a resistance |
| (vii) Heat transfer | (viii) Plastic deformation. |

An irreversible process is usually represented by a dotted (or discontinuous) line joining the end states to indicate that the intermediate states are indeterminate (Fig. 1.29).

Irreversibilities are of two types :

1. **External irreversibilities.** These are associated with dissipating effects outside the working fluid.

Example. Mechanical friction occurring during a process due to some external source.

2. **Internal irreversibilities.** These are associated with dissipating effects within the working fluid.

Example. Unrestricted expansion of gas, viscosity and inertia of the gas.

1.18. ENERGY, WORK AND HEAT

1.18.1. Energy

Energy is a general term embracing *energy in transition* and *stored energy*. The stored energy of a substance may be in the forms of *mechanical energy* and *internal energy* (other forms of stored energy may be chemical energy and electrical energy). Part of the stored energy may take the form of either potential energy (which is the gravitational energy due to height above a chosen datum line) or kinetic energy due to velocity. The balance part of the energy is known as *internal energy*. In a *non-flow process* usually there is no change of potential or kinetic energy and hence change of mechanical energy will not enter the calculations. In a *flow process*, however, there may be changes in both potential and kinetic energy and these must be taken into account while considering the changes of stored energy. *Heat and work* are the forms of energy in transition. These are the only forms in which energy can cross the boundaries of a system. Neither heat nor work can exist as stored energy.

1.18.2. Work and Heat

Work

Work is said to be done when a *force moves through a distance*. If a part of the boundary of a system undergoes a displacement under the action of a pressure, the work done W is the product of the force (pressure \times area), and the distance it moves in the direction of the force. Fig. 1.30 (a)

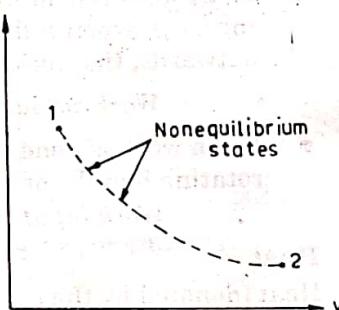


Fig. 1.29. Irreversible process.

rev. edit. by CLASSMATE
illustrates this with the conventional piston and cylinder arrangement, the heavy line defining the boundary of the system. Fig. 1.30 (b) illustrates another way in which work might be applied to a system. A force is exerted by the paddle as it changes the momentum of the fluid, and since this force moves during rotation of the paddle room work is done.

Work is a transient quantity which only appears at the boundary while a change of state is taking place within a system. Work is 'something' which appears at the boundary when a system changes its state due to the movement of a part of the boundary under the action of a force.

Sign convention :

- If the work is done by the system on the surroundings, e.g. when a fluid expands pushing a piston outwards, the work is said to be *positive*.

i.e.

$$\text{Work output of the system} = +W$$

- If the work is done on the system by the surroundings, e.g., when a force is applied to a rotating handle, or to a piston to compress a fluid, the work is said to be *negative*.

i.e.

$$\text{Work input to system} = -W$$

Heat

Heat (denoted by the symbol Q), may be, defined in an analogous way to work as follows :

"Heat is 'something' which appears at the boundary when a system changes its state due to a difference in temperature between the system and its surroundings".

Heat, like work, is a transient quantity which only appears at the boundary while a change is taking place within the system.

It is apparent that neither δW or δQ are exact differentials and therefore any integration of the elemental quantities of work or heat which appear during a change from state 1 to state 2 must be written as

$$\int_1^2 \delta W = W_{1-2} \text{ or } _1 W_2 \text{ (or } W\text{), and}$$

$$\int_1^2 \delta Q = Q_{1-2} \text{ or } _1 Q_2 \text{ (or } Q\text{)}$$

Sign convention :

If the heat flows *into* a system from the surroundings, the quantity is said to be *positive* and, conversely, if heat flows *from* the system to the surroundings it is said to be *negative*.

In other words :

$$\text{Heat received by the system} = +Q$$

$$\text{Heat rejected or given up by the system} = -Q.$$

Comparison of Work and Heat

Similarities :

- (i) Both are *path functions and inexact differentials*.
- (ii) Both are boundary phenomenon i.e. both are recognized at the boundaries of the system as they cross them.

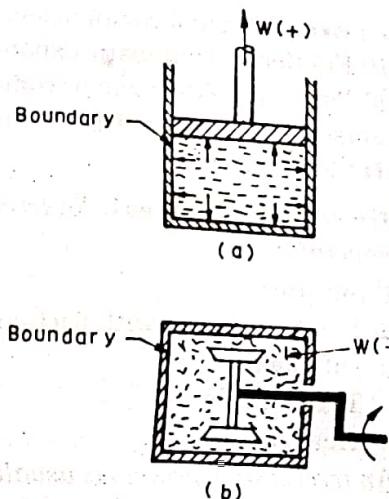


Fig. 1.30

BASIC CONCEPTS OF THERMODYNAMICS

(iii) Both are associated with a process, not a state. Unlike properties, work or heat has no meaning at a state.

(iv) Systems possess energy, but not work or heat.

Dissimilarities :

(i) In heat transfer temperature difference is required.

(ii) In a stable system there cannot be work transfer, however, there is no restriction for the transfer of heat.

(iii) The sole effect external to the system could be reduced to rise of a weight but in the case of a heat transfer other effects are also observed.

1.19. REVERSIBLE WORK

Let us consider an ideal frictionless fluid contained in a cylinder above a piston as shown in Fig. 1.31. Assume that the pressure and temperature of the fluid are uniform and that there is no friction between the piston and the cylinder walls.

Let A = cross-sectional area of the piston,

p = pressure of the fluid at any instant,

$(p - dp)$ A = restraining force exerted by the surroundings on the piston, and

dl = the distance moved by the piston under the action of the force exerted.

Then work done by the fluid on the piston is given by force times the distance moved,

i.e., Work done by the fluid

$$= (pA) \times dl = pdV$$

(where dV = a small increase in volume)

Or considering unit mass

$$\text{Work done} = pdv \quad (\text{where } v = \text{specific volume})$$

This is only true when (a) the process is frictionless and (b) the difference in pressure between the fluid and its surroundings during the process is infinitely small. Hence when a reversible process takes place between state 1 and state 2, we have

Work done by the unit mass of fluid

$$= \int_1^2 pdv \quad \dots(1.10)$$

When a fluid undergoes a reversible process a series of state points can be joined up to form a line on a diagram of properties. The work done by the fluid during any reversible process is therefore given by the area under the line of process plotted on a p - v diagram (Fig. 1.32).

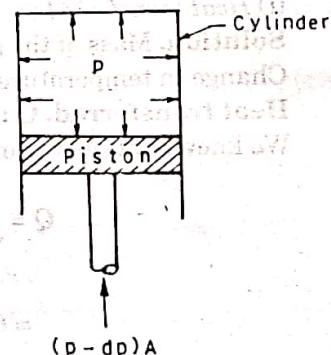


Fig. 1.31

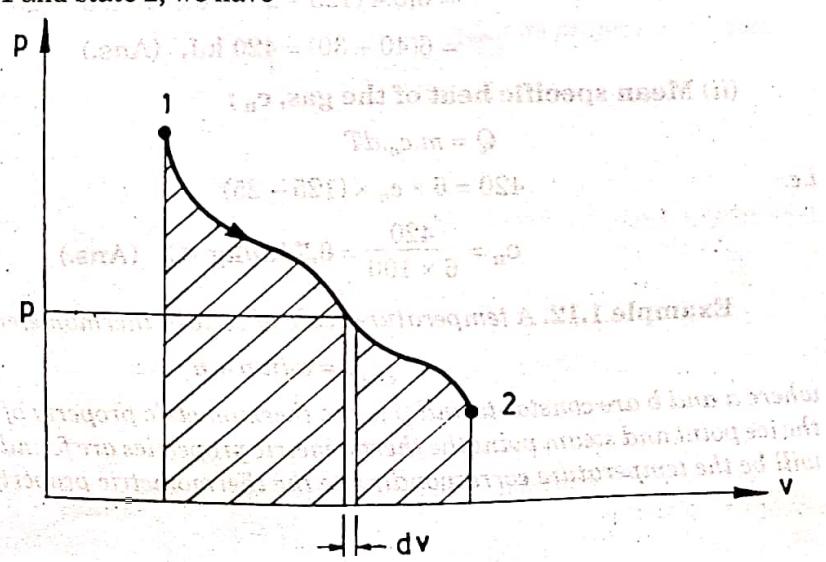


Fig. 1.32

i.e., Work done = shaded area on Fig. 1.32

$$= \int_1^2 p dv.$$

When p can be expressed in terms of v then the integral, $\int_1^2 p dv$, can be evaluated.

Example 1.10. An artificial satellite revolves round the earth with a relative velocity of 800 m/s. If acceleration due to gravity is 9 m/s^2 and gravitational force is 3600 N, calculate its kinetic energy.

Solution. Relatively velocity of satellite, $v = 800 \text{ m/s}$

Acceleration due to gravity, $g = 9 \text{ m/s}^2$

Gravitational force, $m.g = 3600 \text{ N}$

$$\therefore \text{Mass, } m = \frac{3600}{g} = \frac{3600}{9} = 400 \text{ kg.}$$

$$\text{Kinetic energy } = \frac{1}{2} mv^2 = \frac{1}{2} \times 400 \times (800)^2 \text{ J} = 128 \times 10^6 \text{ J or } 128 \text{ MJ. (Ans.)}$$

Example 1.11. The specific heat capacity of the system during a certain process is given by $c_n = (0.4 + 0.004 T) \text{ kJ/kg°C}$.

If the mass of the gas is 6 kg and its temperature changes from 25°C to 125°C find :

- (i) Heat transferred ; (ii) Mean specific heat of the gas.

Solution. Mass of the gas, $m = 6 \text{ kg}$

Change in temperature of the gas = 25°C to 125°C

Heat transferred, Q :

We know that heat transferred is given by,

$$\begin{aligned} Q &= \int m c_n dT = 6 \int_{25}^{125} (0.4 + 0.004 T) dT \\ &= 6 \left[0.4 T + 0.004 \left(\frac{T^2}{2} \right) \right]_{25}^{125} \\ &= 6[0.4(125 - 25) + 0.002(125^2 - 25^2)] \\ &= 6(40 + 30) = 420 \text{ kJ. (Ans.)} \end{aligned}$$

(ii) Mean specific heat of the gas, c_n :

$$Q = m.c_n.dT$$

i.e.

$$420 = 6 \times c_n \times (125 - 25)$$

$$\therefore c_n = \frac{420}{6 \times 100} = 0.7 \text{ kJ/kg°C. (Ans.)}$$

Example 1.12. A temperature scale of certain thermometer is given by the relation

$$t = a \ln p + b$$

where a and b are constants and p is the thermometric property of the fluid in the thermometer. If at the ice point and steam point the thermometric properties are found to be 1.5 and 7.5 respectively what will be the temperature corresponding to the thermometric property of 3.5 on Celsius scale.

(Poona University, Nov. 1997)

BASIC CONCEPTS OF THERMODYNAMICS

Solution. $t = a \ln p + b$

On Celsius scale :

Ice point = 0°C , and

Steam point = 100°C

∴ From given conditions, we have

$$0 = a \ln 1.5 + b \quad \dots(i)$$

$$100 = a \ln 7.5 + b \quad \dots(ii)$$

$$0 = a \times 0.4054 + b \quad \dots(iii)$$

$$100 = a \times 2.015 + b \quad \dots(iv)$$

i.e. and
Subtracting (iii) from (iv), we get

$$100 = 1.61a$$

or

$$a = 62.112$$

Substituting this value in eqn. (iii), we get

$$b = -0.4054 \times 62.112 = -25.18$$

∴ When $p = 3.5$ the value of temperature is given by

$$t = 62.112 \ln (3.5) - 25.18 = 52.63^\circ\text{C}. \quad (\text{Ans.})$$

Example 1.13. A thermocouple with test junction at $t^\circ\text{C}$ on gas thermometer scale and reference junction at ice point gives the e.m.f. as

$$e = 0.20 t - 5 \times 10^{-4} t^2 \text{ mV.}$$

The millivoltmeter is calibrated at ice and steam points. What will be the reading on this thermometer where the gas thermometer reads 70°C .

Solution.

$$e = 0.20 t - 5 \times 10^{-4} t^2 \text{ mV} \quad (\text{given})$$

At ice point : When $t = 0^\circ\text{C}$, $e = 0$

At steam point : When $t = 100^\circ\text{C}$,

$$e = 0.20 \times 100 - 5 \times 10^{-4} \times (100)^2 = 15 \text{ mV}$$

Now,

when $t = 70^\circ\text{C}$

$$e = 0.20 \times 70 - 5 \times 10^{-4} \times (70)^2 = 11.55 \text{ mV}$$

∴ When the gas thermometer reads 70°C the thermocouple will read

$$t = \frac{100 \times 11.55}{15} = 77^\circ\text{C}. \quad (\text{Ans.})$$

Example 1.14. Comment whether the following quantities can be called as properties or not :

$$(i) \int pdV, \quad (ii) \int Vdp, \text{ and} \quad (iii) \int pdV + \int Vdp.$$

Solution. (i) $\int pdV$:

p is a function of V and integral can only be evaluated if relation between p and V is known.

It is thus an *inexact differential* and hence **not a property**.

(ii) $\int Vdp$:

It is **not a property** for the same reason as mentioned in (i).

(iii) $\int pdV + \int Vdp$:

$$\int pdV + \int Vdp = \int (pdV + Vdp) = \int d(pV) = pV.$$

Thus the integral can be evaluated without knowing the relation between p and V . It is an exact differential and hence it is a property.

Example 1.15. Gas from a cylinder of compressed helium is used to inflate an inelastic flexible balloon, originally folded completely flat, to a volume 0.6 m^3 . If the barometer reads 760 mm Hg , what is the amount of work done upon the atmosphere by the balloon? Sketch the system before and after the process.

Solution. Refer Fig. 1.33. The firm line B_1 shows the boundary of the system before the process, and dotted line B_2 shows the boundary after the process.

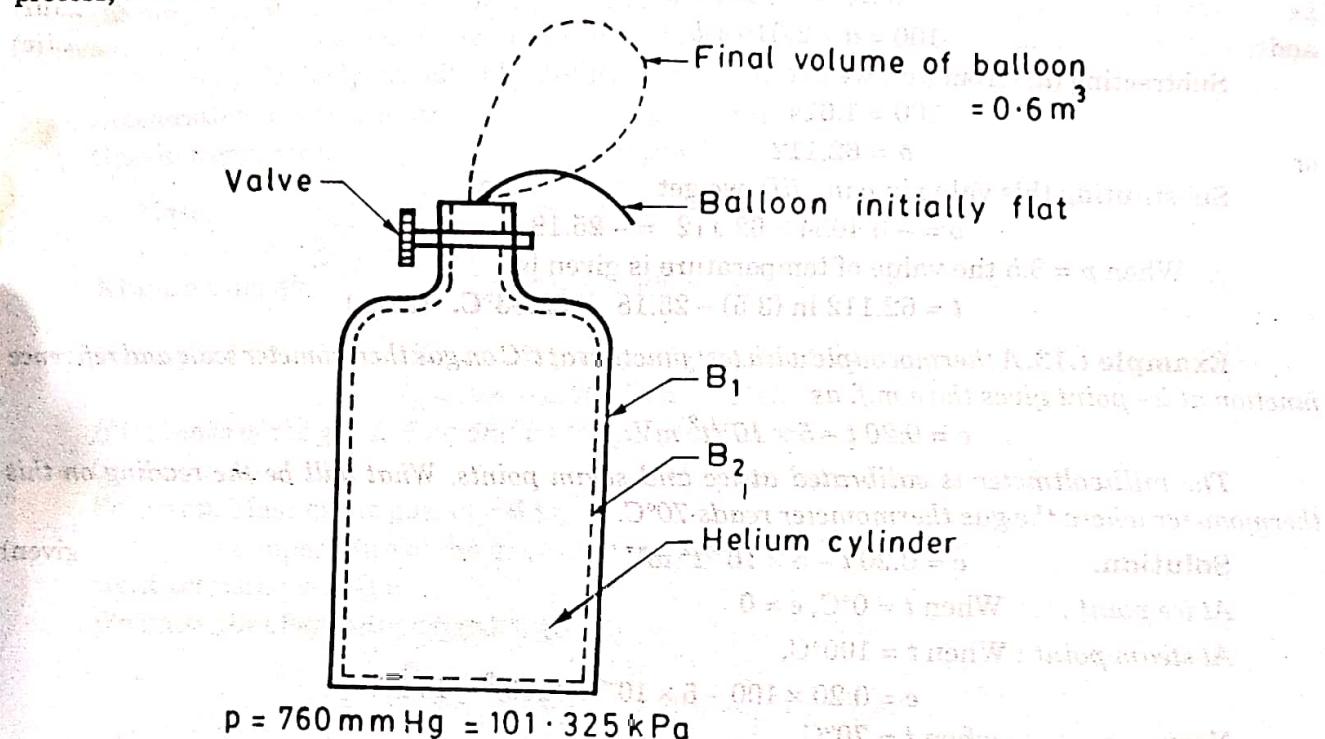


Fig. 1.33

The displacement work,

$$\begin{aligned} W_d &= \int_{\text{cylinder}} p dV + \int_{\text{balloon}} p dV = 0 + \int_{\text{balloon}} p dV \\ &= 101.325 \times 0.6 \\ &= 60.795 \text{ kJ. (Ans.)} \quad [\because dV = 0.6 \text{ m}^3] \end{aligned}$$

This is a positive work, because the work is done by the system. Work done by the atmosphere is -60.795 kJ . Since the wall of the cylinder is rigid there is no pdV -work involved in it. It is assumed that the pressure in the balloon is atmospheric at all times, since the balloon fabric is light, inelastic and unstressed. If the balloon were elastic and stressed during the filling process, the work done by the gas would be greater than 60.795 kJ by an amount equal to the work done in stretching the balloon, although the displacement work done by atmosphere is still -60.795 kJ . However, if the system includes both the gas and the balloon, the displacement work should be 60.795 kJ , as estimated above.

Example 1.16. Determine the work done by the air which enters into an evacuated vessel from atmosphere when the valve is opened. The atmospheric pressure is 1.013 bar and 1.5 m^3 of air at atmospheric condition enters into the vessel.

BASIC CONCEPTS OF THERMODYNAMICS

Solution. Fig. 1.34 shows the initial and final conditions of the system:

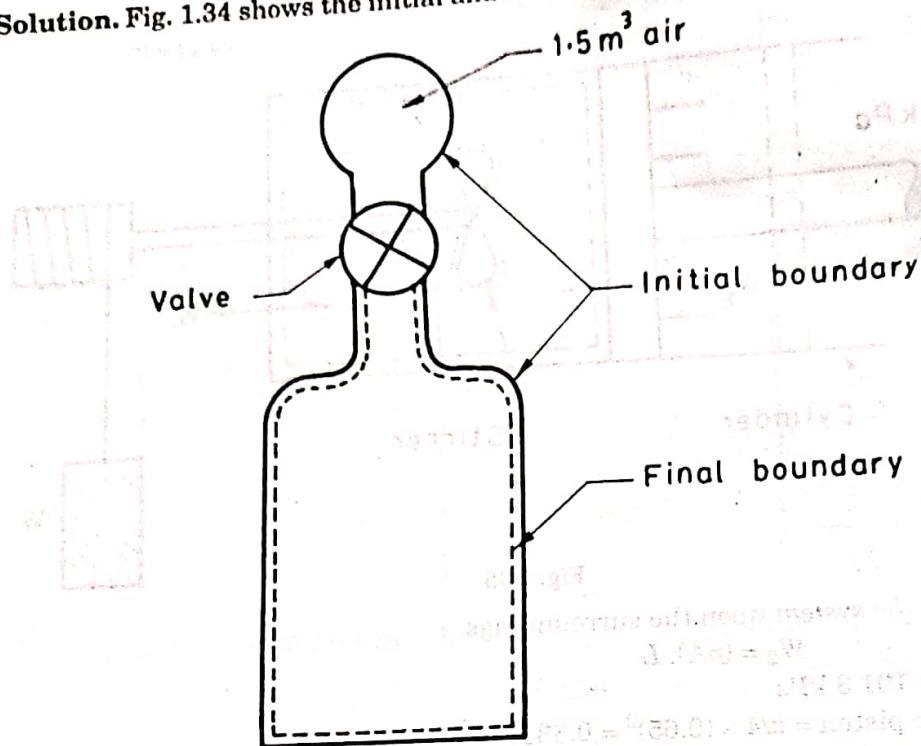


Fig. 1.34

No work is done by the boundary in contact with the vessel as the boundary does not move.

Work is done by the external boundary at constant pressure.

$$\therefore W = \int_{V_1}^{V_2} p dV = \int_{1.5}^0 p dV \quad [\because V_1 = 1.5 \text{ m}^3 \text{ and } V_2 = 0] \\ = p(0 - 1.5) = 1.013 \times 10^5 \times (-1.5) \\ = -1.5195 \times 10^5 \text{ J} = -151.95 \text{ kJ. (Ans.)}$$

Since the free air boundary is contracting, the work done by the system is negative, and the surroundings do positive work upon the system.

Example 1.17. A piston and cylinder machine containing a fluid system has a stirring device as shown in Fig. 1.35. The piston is frictionless, and it is held down against the fluid due to atmospheric pressure of 101.3 kPa. The stirring device is turned 9500 revolutions with an average torque against the fluid of 1.25 mN. Meanwhile the piston of 0.65 m diameter moves out 0.6 m. Find the net work transfer for the system.

Solution. Refer Fig. 1.35.

Work done by the stirring device upon the system,

$$W_1 = 2\pi NT$$

where T = torque = 1.25 mN

N = number of revolutions = 9500

$$W_1 = 2\pi \times 9500 \times 1.25 = 74622 \text{ Nm} = 74.622 \text{ kJ}$$

This is negative work for the system.

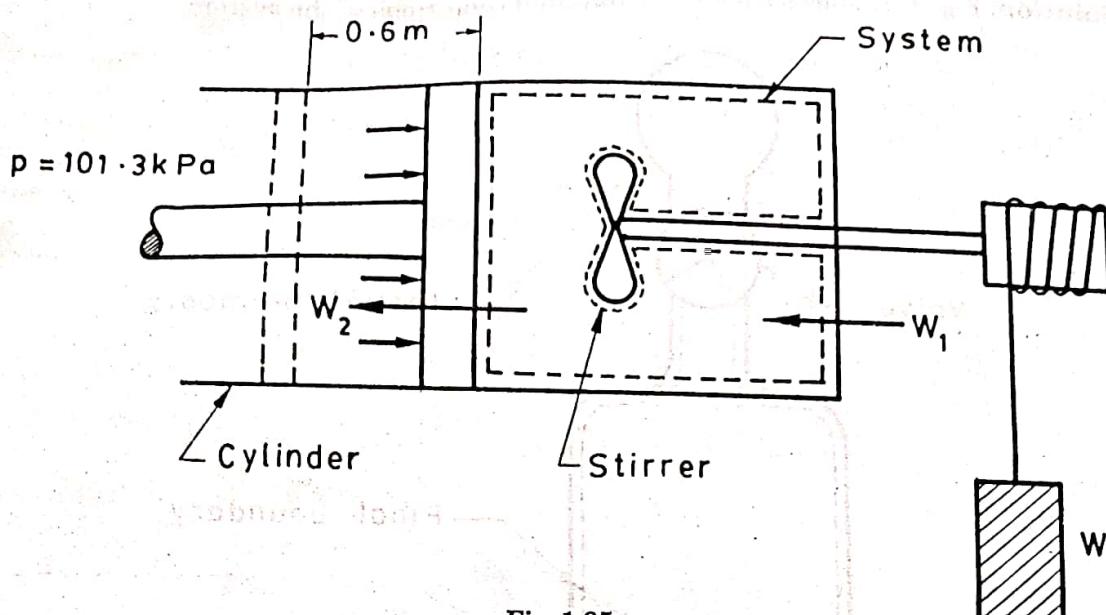


Fig. 1.35

Work done by the system upon the surroundings

$$W_2 = (pA) \cdot L$$

where p = pressure = 101.3 kPa

$$A = \text{area of the piston} = \pi/4 \times (0.65)^2 = 0.3318 \text{ m}^2$$

$$L = \text{distance moved by the piston} = 0.6 \text{ m}$$

$$W_2 = 101.3 \times 0.3318 \times 0.6 = 20.167 \text{ kJ}$$

This is a positive work for the system.

Hence, the net work transfer for the system

$$W_{\text{net}} = W_1 + W_2 = -74.622 + 20.167 = -54.455 \text{ kJ. (Ans.)}$$

Example 1.18. A diesel engine piston which has an area of 45 cm^2 moves 5 cm during part of suction stroke. 300 cm^3 of fresh air is drawn in from the atmosphere. The pressure in the cylinder during suction stroke is $0.9 \times 10^5 \text{ N/m}^2$ and the atmospheric pressure is $1.013 \times 10^5 \text{ N/m}^2$. The difference between the suction and atmospheric pressure is accounted for flow resistance in the suction pipe and inlet valve. Find the net work done during the process.

Solution. Area of diesel engine piston

$$= 45 \text{ cm}^2 = 45 \times 10^{-4} \text{ m}^2$$

Amount of fresh air drawn in from atmosphere

$$= 300 \text{ cm}^3 = 300 \times 10^{-6} \text{ m}^3$$

The pressure inside the cylinder during suction stroke

$$= 0.9 \times 10^5 \text{ N/m}^2$$

$$\text{Atmospheric pressure} = 1.013 \times 10^5 \text{ N/m}^2$$

Initial and final conditions of the system are shown in Fig. 1.36.

Net work done = work done by free air boundary + work done on the piston

The work done by the free air = -ve because boundary contracts

The work done by the cylinder on the piston = +ve because the boundary expands

BASIC CONCEPTS OF THERMODYNAMICS

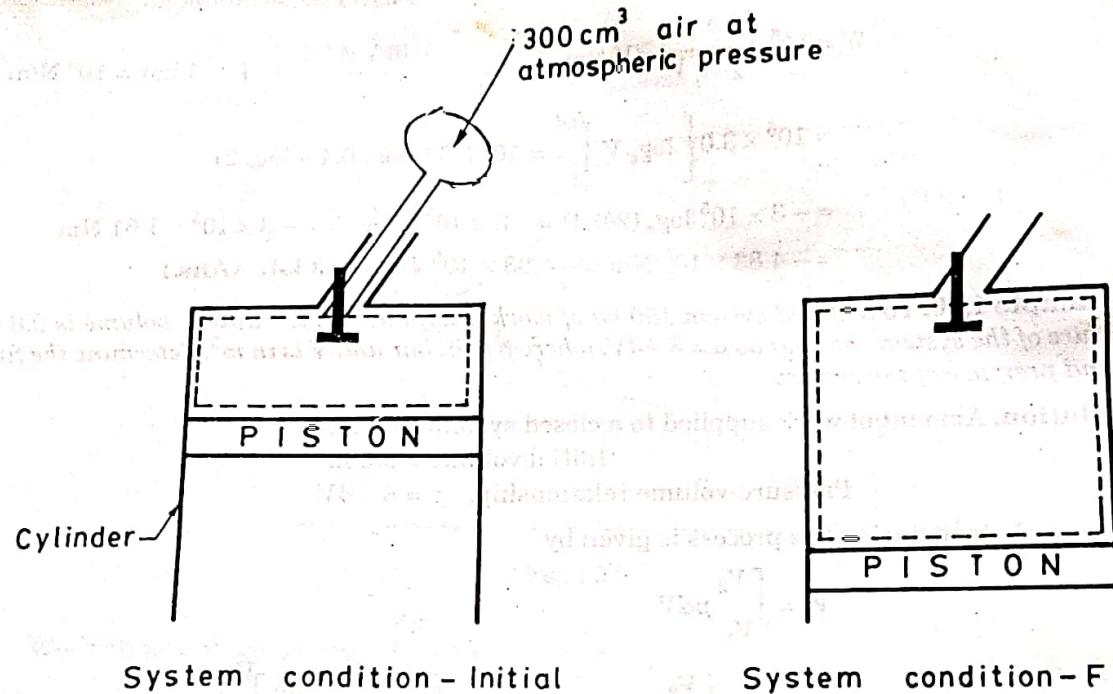


Fig. 1.36

$$\therefore \text{Net work done} = \int_{\text{piston}}^{45 \times 10^{-4}} pdV + \int_{\text{free air}}^{\text{boundary}} pdV$$

$$= \left[0.9 \times 10^5 \times 45 \times 10^{-4} \times \frac{5}{100} - 1.013 \times 10^5 \times 300 \times 10^{-6} \right]$$

$$= [20.25 - 30.39] = -10.14 \text{ Nm or J. (Ans.)}$$

Example 1.19. The properties of a closed system change following the relation between pressure and volume as $pV = 3.0$ where p is in bar V is in m^3 . Calculate the work done when the pressure increases from 1.5 bar to 7.5 bar.

Solution. Initial pressure, $p_1 = 1.5 \text{ bar}$

Final pressure, $p_2 = 7.5 \text{ bar}$

Relation between p and V , $pV = 3.0$

Work done,

$W :$

The work done during the process is given by

$$W = \int_{V_1}^{V_2} pdV$$

$$V_1 = \frac{3.0}{p_1} = \frac{3.0}{1.5} = 2 \text{ m}^3$$

$$V_2 = \frac{3.0}{p_2} = \frac{3.0}{7.5} = 0.4 \text{ m}^3$$

$$\begin{aligned}
 W &= 10^5 \int_2^{0.4} \frac{3.0}{V} dV \text{ Nm} \\
 &= 10^5 \times 3.0 \left[\log_e V \right]_2^{0.4} = 10^5 \times 3.0 (\log_e 0.4 - \log_e 2) \\
 &= -3 \times 10^5 \log_e (2/0.4) = -3 \times 10^5 \times \log_e 5 = -3 \times 10^5 \times 1.61 \text{ Nm} \\
 &= -4.83 \times 10^5 \text{ Nm} = -4.83 \times 10^5 \text{ J} = -483 \text{ kJ. (Ans.)}
 \end{aligned}$$

Example 1.20. To a closed system 150 kJ of work is supplied. If the initial volume is 0.6 m^3 and pressure of the system changes as $p = 8 - 4V$, where p is in bar and V is in m^3 , determine the final volume and pressure of the system.

Solution. Amount of work supplied to a closed system = 150 kJ

$$\begin{aligned}
 \text{Initial volume} &= 0.6 \text{ m}^3 \\
 \text{Pressure-volume relationship, } p &= 8 - 4V
 \end{aligned}$$

The work done during the process is given by

$$W = \int_{V_1}^{V_2} p dV$$

$$\begin{aligned}
 &= 10^5 \int_{0.6}^{V_2} (8 - 4V) dV = 10^5 \left[8V - 4 \times \frac{V^2}{2} \right]_{0.6}^{V_2} \\
 &= 10^5 [8(V_2 - 0.6) - 2(V_2^2 - 0.6^2)] \\
 &= 10^5 [8V_2 - 4.8 - 2V_2^2 + 0.72] \\
 &= 10^5 [8V_2 - 2V_2^2 - 4.08] \text{ Nm or J}
 \end{aligned}$$

But this work is equal to $-150 \times 10^3 \text{ J}$ as this work is supplied to the system.

$$\therefore -150 \times 10^3 = 10^5 [8V_2 - 2V_2^2 - 4.08]$$

$$\text{or } 2V_2^2 - 8V_2 + 2.58 = 0$$

$$V_2 = \frac{8 \pm \sqrt{64 - 4 \times 2 \times 2.58}}{4} = \frac{8 \pm 6.585}{4} = 0.354 \text{ m}^3$$

Positive sign is incompatible with the present problem, therefore it is not considered.

$$\therefore \text{Final volume, } V_2 = 0.354 \text{ m}^3. \text{ (Ans.)}$$

$$\text{and } \text{final pressure, } p_2 = 8 - 4V = 8 - 4 \times 0.354$$

$$\Rightarrow 6.584 \text{ bar} = 6.584 \times 10^5 \text{ N/m}^2 \text{ or Pa. (Ans.)}$$

Example 1.21. A fluid at a pressure of 3 bar , and with specific volume of $0.18 \text{ m}^3/\text{kg}$, contained in a cylinder behind a piston expands reversibly to a pressure of 0.6 bar according to a law, $p = \frac{C}{v^2}$ where C is a constant. Calculate the work done by the fluid on the piston. (PTU, Jan. 2002)

Solution. Refer Fig. 1.37.

$$p_1 = 3 \text{ bar} = 3 \times 10^5 \text{ N/m}^2$$

$$v_1 = 0.18 \text{ m}^3/\text{kg}$$

BASIC CONCEPTS OF THERMODYNAMICS

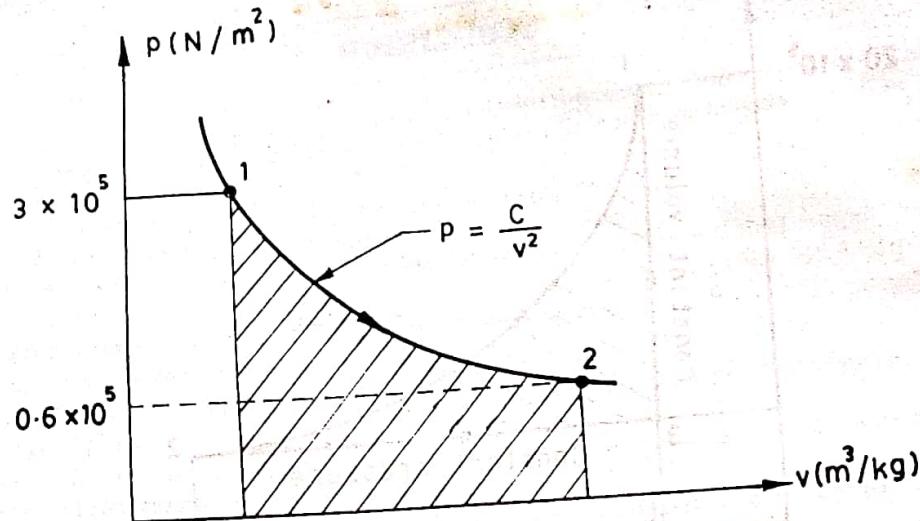


Fig. 1.37

$$\text{Work done} = \text{shaded area} = \int_{v_1}^{v_2} p \, dv$$

$$\begin{aligned} \text{Work done, } W &= \int_{v_1}^{v_2} \frac{C}{v^2} \cdot dv = C \int_{v_1}^{v_2} \frac{dv}{v^2} = C \left| \frac{v^{-2+1}}{-2+1} \right|_{v_1}^{v_2} \\ &= C \left[-v^{-1} \right]_{v_1}^{v_2} = C \left[-\frac{1}{v} \right]_{v_1}^{v_2} = C \left[\frac{1}{v_1} - \frac{1}{v_2} \right] \end{aligned} \quad \dots(i)$$

$$\text{Also } C = pv^2 = p_1v_1^2 = 3 \times 0.18^2 = 0.0972 \text{ bar (m}^3/\text{kg})^2$$

and

$$v_2 = \sqrt{\frac{C}{p_2}} = \sqrt{\frac{0.0972}{0.6}} = 0.402 \text{ m}^3/\text{kg}$$

Substituting the values of C , v_1 and v_2 in equation (i), we get

$$\begin{aligned} \text{Work done, } W &= 0.0972 \times 10^5 \left[\frac{1}{0.18} - \frac{1}{0.402} \right] \text{ Nm/kg} \\ &= 29840 \text{ Nm/kg. (Ans.)} \end{aligned}$$

Example 1.22. A cylinder contains 1 kg of a certain fluid at an initial pressure of 20 bar. The fluid is allowed to expand reversibly behind a piston according to a law $pV^2 = \text{constant}$ until the volume is doubled. The fluid is then cooled reversibly at constant pressure until the piston regains its original position; heat is then supplied reversibly with the piston firmly locked in position until the pressure rises to the original value of 20 bar. Calculate the net work done by the fluid, for an initial volume of 0.05 m^3 .

Solution. Refer Fig. 1.38.

Mass of fluid,

$$m = 1 \text{ kg}$$

$$p_1 = 20 \text{ bar} = 20 \times 10^5 \text{ N/m}^2$$

$$V_1 = 0.05 \text{ m}^3$$

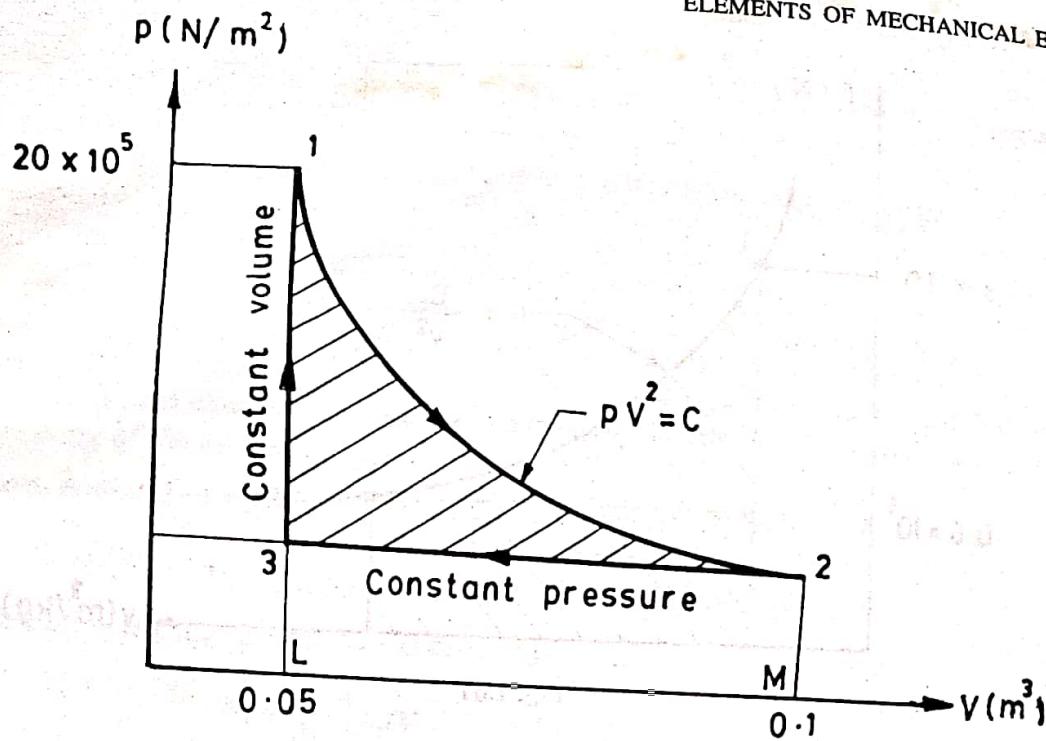


Fig. 1.38

Considering the process 1-2

$$p_1 V_1^2 = p_2 V_2^2$$

$$\therefore p_2 = p_1 \left(\frac{V_1}{V_2} \right)^2 = 20 \left(\frac{V_1}{2V_1} \right)^2 = \frac{20}{4} = 5 \text{ bar}$$

[∴ $V_2 = 2V_1$ (given)]

Work done by the fluid from 1 to 2 = Area 12 ML1 = $\int_1^2 p dV$

$$\text{i.e., } W_{1-2} = \int_{V_1}^{V_2} \frac{C}{V^2} dV, \text{ where } C = p_1 V_1^2 = 20 \times 0.05^2 \text{ bar m}^6$$

$$\therefore W_{1-2} = 10^5 \times 20 \times 0.0025 \left[-\frac{1}{V} \right]_{0.05}^{0.1}$$

$$= 10^5 \times 20 \times 0.0025 \left(\frac{1}{0.05} - \frac{1}{0.1} \right) = 50000 \text{ Nm}$$

Work done on fluid from 2 to 3

$$= \text{Area } 32 \text{ ML } 3 = p_2 (V_2 - V_3) = 10^5 \times 5 \times (0.1 - 0.05) = 25000 \text{ Nm}$$

Work done during the process 3-1

= 0, because piston is locked in position

∴ Net work done by the fluid

$$= \text{Enclosed area } 1231 = 50000 - 25000$$

$$= 25000 \text{ Nm. (Ans.)}$$

2

First Law of Thermodynamics

2.1. Internal energy. 2.2. Law of conservation of energy. 2.3. First law of thermodynamics. 2.4. Application of first law to a process. 2.5. Energy—a property of system. 2.6. Perpetual motion machine of the first kind—PMM1. 2.7. Energy of an isolated system. 2.8. The perfect gas—The characteristic equation of state—Specific heats—Joule's law—Relationship between two specific heats—Enthalpy—Ratio of specific heats. 2.9. Application of First law of thermodynamics to non-flow or closed system. 2.10. Application of first law to steady flow process. 2.11. Energy relations for flow process. 2.12. Engineering applications of steady flow energy equation (S.F.E.E.)—Water turbine—Steam or Gas turbine—Centrifugal water pump—Centrifugal compressor—Reciprocating compressor—Boiler—Condenser—Evaporator—Steam nozzle. 2.13. Throttling process and Joule-Thompson porous plug experiment. 2.14. Heating-Cooling and expansion of vapours. 2.15. Unsteady flow processes—Highlights—Objective Type Questions—Theoretical Questions—Unsolved Examples.

2.1. INTERNAL ENERGY

It is the heat energy stored in a gas. If a certain amount of heat is supplied to a gas the result is that temperature of gas may increase or volume of gas may increase thereby doing some external work or both temperature and volume may increase ; but it will be decided by the conditions under which the gas is supplied heat. *If during heating of the gas the temperature increases its internal energy will also increase.*

Joule's law of internal energy states that internal energy of a perfect gas is a function of temperature only. In other words, internal energy of a gas is dependent on the temperature change only and is not affected by the change in pressure and volume.

We do not know how to find the absolute quantity of internal energy in any substance ; however, what is needed in engineering is the change of internal energy (ΔU).

2.2. LAW OF CONSERVATION OF ENERGY

In the early part of nineteenth century the scientists developed the concept of energy and hypothesis that it can be neither created nor destroyed ; this came to be known as the *law of the conservation of energy*. The first law of thermodynamics is merely one statement of this general law/principle with particular reference to heat energy and mechanical energy i.e. work.

2.3. FIRST LAW OF THERMODYNAMICS

It is observed that when a system is made to undergo a complete cycle then net work is done on or by the system. Consider a cycle in which net work is done by the system. Since energy cannot be created, this mechanical energy must have been supplied from some source of energy. Now the system has been returned to its initial state : Therefore, its intrinsic energy is unchanged, and hence the mechanical energy has not been provided by the system itself. The only other energy involved in the cycle is the heat which was supplied and rejected in various processes. Hence, by the law of conservation of energy, the net work done by the system is equal to the net heat supplied to the system. The First Law of Thermodynamics can, therefore, be stated as follows :

When a system undergoes a thermodynamic cycle then the net heat supplied to the system from the surroundings is equal to net work done by the system on its surroundings.

or

$$\oint dQ = \oint dW$$

where \oint represents the sum for a complete cycle.

The first law of Thermodynamics *cannot be proved analytically, but experimental evidence has repeatedly confirmed its validity*, and since no phenomenon has been shown to contradict it, the first law is accepted as a *law of nature*. It may be remarked that no restriction was imposed which limited the application of first law to reversible energy transformation. Hence the first law applies to reversible as well as irreversible transformations : For non-cyclic process, a more general formulation of first law of thermodynamics is required. A new concept which involves a term called *internal energy* fulfills this need.

— The First Law of Thermodynamics may also be stated as follows :

"Heat and work are mutually convertible but since energy can neither be created nor destroyed, the total energy associated with an energy conversion remains constant".

Or

— "No machine can produce energy without corresponding expenditure of energy, i.e. it is impossible to construct a perpetual motion machine of first kind".

Fig. 2.1 shows the experiment for checking first law of thermodynamics.

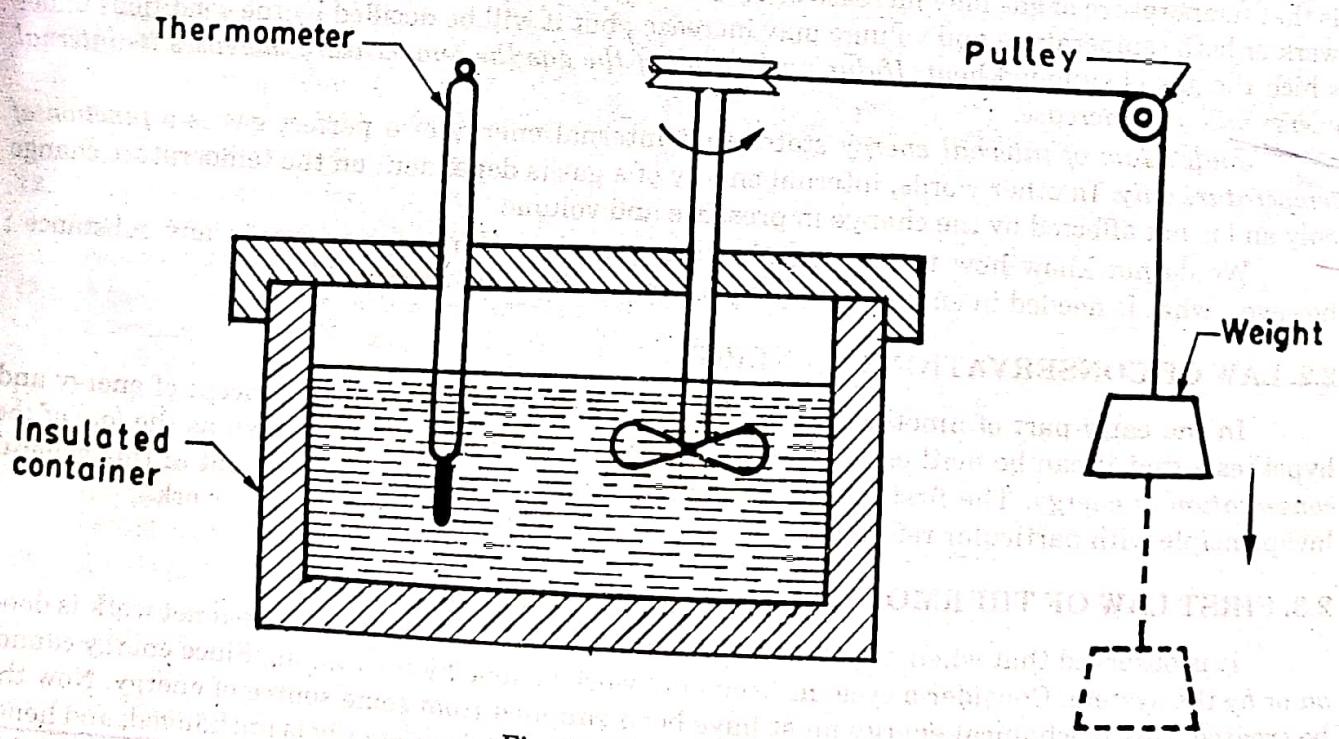


Fig. 2.1. Heat and work.

The work input to the paddle wheel is measured by the fall of weight, while the corresponding temperature rise of liquid in the insulated container is measured by the thermometer. It is already known to us from experiments on heat transfer that temperature rise can also be produced by heat transfer. The experiments show : (i) A definite quantity of work is always required to accomplish the same temperature rise obtained with a unit amount of heat. (ii) Regardless of whether the tempera-

✓

FIRST LAW OF THERMODYNAMICS

ture of liquid is raised by work transfer or heat transfer, the liquid can be returned by heat transfer in opposite direction to the identical state from which it started. The above results lead to the inference that *work and heat* are different forms of something more general, which is called *energy*.

— It can be stated as an invariable experience that whenever a physical system passes through a complete cycle the algebraic sum of the work transfers during the cycle $\oint dW$

bears a definite ratio to the algebraic sum of the heat transfers during the cycle, $\oint dQ$.

This may be expressed by the equation,

$$\oint dW = J \oint dQ \quad \dots(2.1)$$

where J is the proportionality constant and is known as *Mechanical Equivalent of heat*. In S.I. units its value is unity, i.e., 1 Nm/J .

2.4. APPLICATION OF FIRST LAW TO A PROCESS

When a process is executed by a system, the *change in stored energy of the system is numerically equal to the net heat interactions minus the net work interaction during the process*.

$$\begin{aligned} E_2 - E_1 &= Q - W \\ \Delta E &= Q - W \quad [\text{or } Q = \Delta E + W] \end{aligned}$$

or

$$\int_1^2 d(Q - W) = \Delta E = E_2 - E_1 \quad \dots(2.2)$$

where E represents the *total internal energy*.

If the electric, magnetic and chemical energies are *absent* and changes in potential and kinetic energy for a *closed system* are neglected, the above equation can be written as

$$\int_1^2 d(Q - W) = \Delta U = U_2 - U_1 \quad \dots(2.3)$$

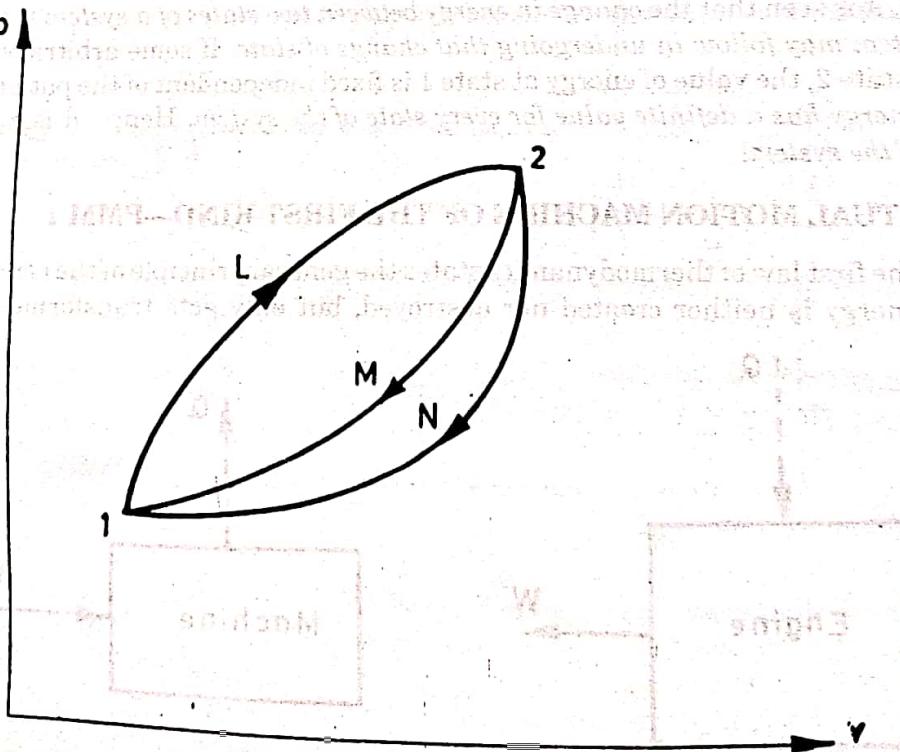


Fig. 2.2. Energy—a property of system.

$$\therefore Q - W = \Delta U = U_2 - U_1 \quad \dots(2.4)$$

Generally, when heat is added to a system its temperature rises and external work is performed due to increase in volume of the system. The rise in temperature is an indication of increase of internal energy.

Heat added to the system will be considered as positive and the heat removed or rejected, from the system, as negative.

2.5. ENERGY—A PROPERTY OF SYSTEM

Consider a system which changes its state from state 1 to state 2 by following the path L , and returns from state 2 to state 1 by following the path M (Fig. 2.2). So the system undergoes a cycle. Writing the first law for path L

$$Q_L = \Delta E_L + W_L \quad \dots(2.5)$$

and for path M

$$Q_M = \Delta E_M + W_M \quad \dots(2.6)$$

The processes L and M together constitute a cycle, for which

$$\oint dW = \oint dQ$$

$$W_L + W_M = Q_L + Q_M$$

$$Q_L - W_L = W_M - Q_M$$

From equations (2.5), (2.6) and (2.7), it yields

$$\Delta E_L = -\Delta E_M \quad \dots(2.8)$$

Similarly, had the system returned from state 2 to state 1 by following the path N instead of path M

$$\Delta E_L = -\Delta E_N \quad \dots(2.9)$$

From equations (2.8) and (2.9),

$$\Delta E_M = \Delta E_N \quad \dots(2.10)$$

Thus, it is seen that the change in energy between two states of a system is the same, whatever path the system may follow in undergoing that change of state. If some arbitrary value of energy is assigned to state 2, the value of energy at state 1 is fixed independent of the path the system follows. Therefore, energy has a definite value for every state of the system. Hence, it is a point function and a property of the system.

2.6. PERPETUAL MOTION MACHINE OF THE FIRST KIND—PMM 1

- The first law of thermodynamics states the general principle of the conservation of energy. Energy is neither created nor destroyed, but only gets transformed from one form to

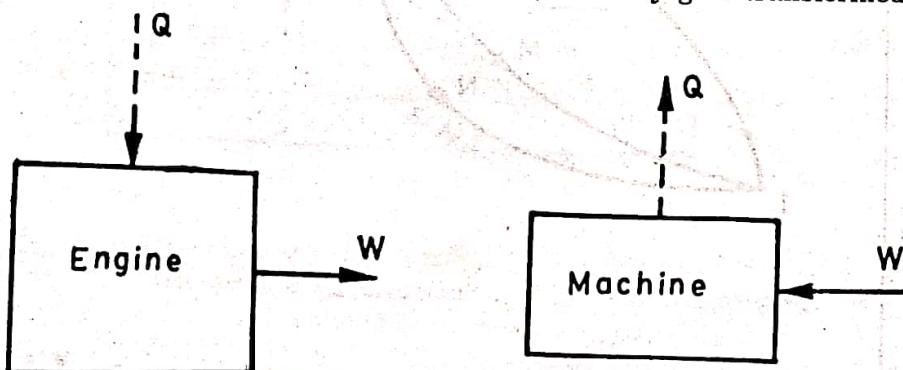


Fig. 2.3. A PMM 1.

Fig. 2.4. The converse of PMM 1.

FIRST LAW OF THERMODYNAMICS

another. There can be no machine which would continuously supply mechanical work without some form of energy disappearing simultaneously (Fig. 2.3). Such a fictitious machine is called a *perpetual motion machine of the first kind*, or in brief, PMM 1. A PMM 1 is thus impossible.

- The converse of the above statement is also true, i.e., there can be no machine which would continuously consume work without some other form of energy appearing simultaneously (Fig. 2.4).

2.7. ENERGY OF AN ISOLATED SYSTEM

An isolated system is one in which there is no interaction of the system with the surroundings.

For an isolated system,

$$dQ = 0, dW = 0$$

The first law of thermodynamics gives

$$dE = 0$$

$$E = \text{constant}$$

or

The energy of an isolated system is always constant.

2.8. THE PERFECT GAS

2.8.1. The Characteristic Equation of State

- At temperatures that are considerably in excess of critical temperature of a fluid, and also at very low pressure, the vapour of fluid tends to obey the equation

$$\frac{pv}{T} = \text{constant} = R$$

In practice, no gas obeys this law rigidly, but many gases tend towards it.

An imaginary ideal gas which obeys this law is called a *perfect gas*, and the equation $\frac{pv}{T} = R$,

is called the *characteristic equation of a state of a perfect gas*. The constant R is called the *gas constant*. Each perfect gas has a different gas constant.

Units of R are Nm/kg K or kJ/kg K.

Usually, the characteristic equation is written as

$$pv = RT \quad \dots(2.11)$$

or for m kg, occupying V m³

$$pV = mRT \quad \dots(2.12)$$

- The characteristic equation in another form, can be derived by using kilogram-mole as a unit.

The *kilogram-mole* is defined as a quantity of a gas equivalent to M kg of the gas, where M is the molecular weight of the gas (e.g. since the molecular weight of oxygen is 32, then 1 kg mole of oxygen is equivalent to 32 kg of oxygen).

As per definition of the kilogram-mole, for m kg of a gas, we have

$$m = nM \quad \dots(2.13)$$

where n = number of moles.

Note. Since the standard of mass is the kg, kilogram-mole will be written simply as mole.

Substituting for m from Eqn. (2.13) in Eqn. (2.12) gives

$$pV = nMRT$$

or

$$MR = \frac{pV}{nT}$$

According to Avogadro's hypothesis the volume of 1 mole of any gas is the same as the volume of 1 mole of any other gas, when the gases are at the same temperature and pressure. Therefore, $\frac{V}{n}$ is the same for all gases at the same value of p and T . That is the quantity $\frac{pV}{nT}$ is a constant for all gases. This constant is called *universal gas constant*, and is given the symbol, R_0 . i.e.,

$$MR = R_0 = \frac{pV}{nT}$$

or

$$pV = nR_0 T$$

Since $MR = R_0$, then

$$R = \frac{R_0}{M} \quad \dots(2.14)$$

It has been found experimentally that the volume of 1 mole of any perfect gas at 1 bar and 0°C is approximately 22.71 m³.

Therefore from Eqn. (2.14),

$$\begin{aligned} R_0 &= \frac{pV}{nT} = \frac{1 \times 10^5 \times 22.71}{1 \times 273.15} \\ &= 8314.3 \text{ Nm/mole K} \end{aligned}$$

Using Eqn. (2.15), the gas constant for any gas can be found when the molecular weight is known.

Example. For oxygen which has a molecular weight of 32, the gas constant

$$R = \frac{R_0}{M} = \frac{8314}{32} = 259.8 \text{ Nm/kg K.} \checkmark$$

2.8.2. Specific Heats

- The specific heat of a solid or liquid is usually defined as the *heat required to raise unit mass through one degree temperature rise*.
- For small quantities, we have

$$dQ = mcDT$$

where m = mass

c = specific heat

dT = temperature rise.

(For a gas there are an infinite number of ways in which heat may be added between any two temperatures, and hence a gas could have an infinite number of specific heats. However, only two specific heats for gases are defined.)

Specific heat at constant volume, c_v
and Specific heat at constant pressure, c_p .

We have

$$dQ = m c_p dT \quad \text{For a reversible non-flow process at constant pressure} \quad \dots(2.16)$$

$$dQ = m c_v dT \quad \text{For a reversible non-flow process at constant volume} \quad \dots(2.17)$$

The values of c_p and c_v , for a perfect gas, are constant for any one gas at all pressures and temperatures. Hence, integrating Eqns. (2.16) and (2.17), we have

Flow of heat in a reversible constant pressure process

$$= mc_p (T_2 - T_1) \quad \dots(2.18)$$

Flow of heat in a reversible constant volume process

$$= mc_v (T_2 - T_1) \quad \dots(2.19)$$

In case of real gases, c_p and c_v vary with temperature, but a suitable average value may be used for most practical purposes.

FIRST LAW OF THERMODYNAMICS

2.8.3. Joule's Law

Joule's law states as follows :

"The internal energy of a perfect gas is a function of the absolute temperature only."

i.e.,

To evaluate this function let 1 kg of a perfect gas be heated at constant volume.

According to non-flow energy equation,

$$u = f(T)$$

$$\frac{dQ}{dW} = du + dW = 0$$

$$dW = 0, \text{ since volume remains constant}$$

$$dQ = du$$

At constant volume for a perfect gas, from Eqn. (2.17), for 1 kg

$$dQ = c_v dT$$

$$dQ = du = c_v dT$$

$$u = c_v T + K, K \text{ being constant.}$$

and integrating

According to Joule's law $u = f(T)$, which means that internal energy varies linearly with absolute temperature. Internal energy can be made zero at any arbitrary reference temperature. For a perfect gas it can be assumed that $u = 0$ when $T = 0$, hence constant K is zero.

i.e. Internal energy, $u = c_v T$ for a perfect gas

or For mass m , of a perfect gas

$$\text{Internal energy, } U = mc_v T \quad \dots(2.20)$$

For a perfect gas, in any process between states 1 and 2, we have from Eqn. (2.21)

Gain in internal energy, $\Delta U = U_2 - U_1 = mc_v (T_2 - T_1) \quad \dots(2.22)$

$$U_2 - U_1 = mc_v (T_2 - T_1)$$

Eqn. (2.22) gives the gains of internal energy for a perfect gas between two states for any process, reversible or irreversible.

2.8.4. Relationship Between Two Specific Heats

Consider a perfect gas being heated at constant pressure from T_1 to T_2 .

According to non-flow equation,

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

Also for a perfect gas,

$$U_2 - U_1 = mc_v (T_2 - T_1)$$

$$Q = mc_v (T_2 - T_1) + W$$

In a constant pressure process, the work done by the fluid,

$$W = p(V_2 - V_1)$$

$$= mR(T_2 - T_1)$$

$$dQ = dU + dW$$

$$\therefore p_1V_1 = mRT_1$$

$$p_2V_2 = mRT_2$$

$$p_1 = p_2 = p \text{ in this case}$$

On substituting

$$Q = mc_v (T_2 - T_1) + mR(T_2 - T_1) = m(c_v + R)(T_2 - T_1)$$

But for a constant pressure process,

$$Q = mc_p (T_2 - T_1)$$

By equating the two expressions, we have

$$m(c_v + R)(T_2 - T_1) = mc_p(T_2 - T_1)$$

∴

$$c_v + R = c_p$$

$$c_p - c_v = R$$

$$\dots(2.23)$$

Dividing both sides by c_v , we get

$$\frac{c_p}{c_v} - 1 = \frac{R}{c_v}$$

$$\therefore c_v = \frac{R}{\gamma - 1}$$

(where $\gamma = c_p/c_v$)

...[2.23 (a)]

Similarly, dividing both sides by c_p , we get

$$c_p = \frac{\gamma R}{\gamma - 1}$$

...[2.23 (b)]

$$\left[\begin{array}{l} \text{In M.K.S. units : } c_p - c_v = \frac{R}{J}; c_v = \frac{R}{J(\gamma - 1)}, c_p = \frac{\gamma R}{(\gamma - 1)J} \\ \text{In SI units the value of } J \text{ is unity.} \end{array} \right]$$

2.8.5. Enthalpy

- One of the fundamental quantities which occur invariably in thermodynamics is the sum of internal energy (u) and pressure volume product (pv). This sum is called **Enthalpy** (h).
$$h = u + pv \quad \dots(2.24)$$
- The enthalpy of a fluid is the property of the fluid, since it consists of the sum of a property and the product of the two properties. Since enthalpy is a property like internal energy, pressure, specific volume and temperature, it can be introduced into any problem whether the process is a flow or a non-flow process.

The total enthalpy of mass, m , of a fluid can be

$$H = U + pV, \text{ where } H = mh.$$

For a perfect gas,

Referring equation (2.24),

$$\begin{aligned} h &= u + pv \\ &= c_v T + RT \\ &\equiv (c_v + R)T \\ &= c_p T \\ h &= c_p T \\ H &= mc_p T. \end{aligned} \quad [\because c_p = c_v + R]$$

i.e.,
and

(Note that, since it has been assumed that $u = 0$ at $T = 0$, then $h = 0$ at $T = 0$).

2.8.6. Ratio of Specific Heats

The ratio of specific heat at constant pressure to the specific heat at constant volume is given the symbol γ (gamma).

i.e.,

$$\gamma = \frac{c_p}{c_v} \quad \dots(2.25)$$

Since $c_p = c_v + R$, it is clear that c_p must be greater than c_v for any perfect gas. It follows, therefore, that the ratio, $\frac{c_p}{c_v} = \gamma$ is always greater than unity.

In general, the approximate values of γ are as follows :

For monoatomic gases such as argon, helium = 1.6.

For diatomic gases such as carbon monoxide, hydrogen, nitrogen and oxygen = 1.4.

For triatomic gases such as carbondioxide and sulphur dioxide = 1.3.

For some hydro-carbons the value of γ is quite low.

[e.g., for ethane $\gamma = 1.22$, and for isobutane $\gamma = 1.11$]

2.9. APPLICATION OF FIRST LAW OF THERMODYNAMICS TO NON-FLOW OR CLOSED SYSTEM

(1) Reversible Constant Volume Process ($v = \text{constant}$)—*Isochoric process*

In a constant volume process the working substance is contained in a rigid vessel, hence the boundaries of the system are immovable and no work can be done on or by the system, other than paddle-wheel work input. It will be assumed that 'constant volume' implies zero work unless stated otherwise.

Fig. 2.5 shows the system and states before and after the heat addition at constant volume.

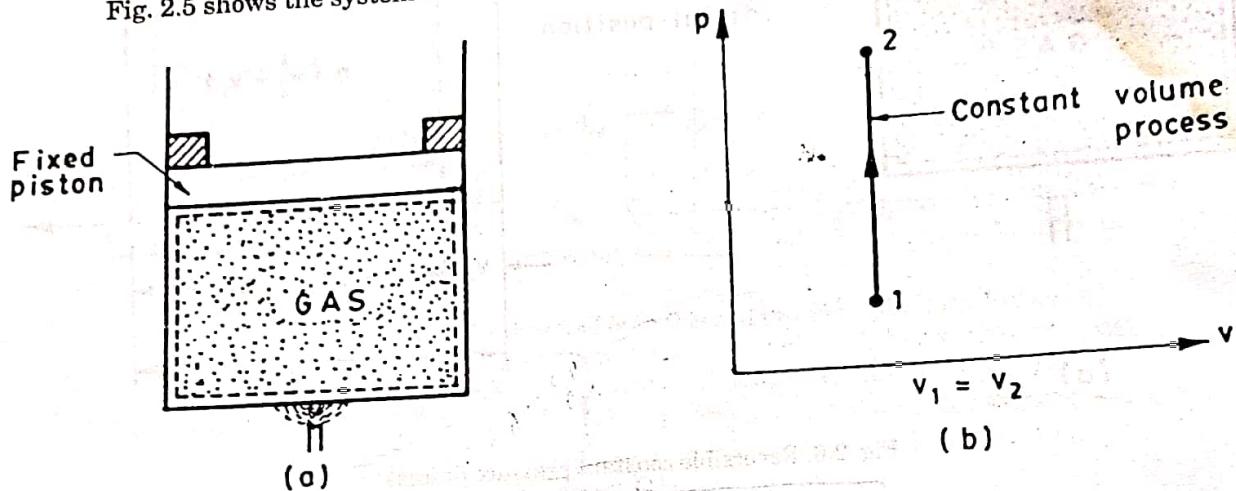


Fig. 2.5. Reversible constant volume process.

Considering mass of the working substance *unity* and applying first law of thermodynamics to the process

$$Q = (u_2 - u_1) + W \quad \dots(2.26)$$

The work done

$$W = \int_1^2 pdv = 0 \text{ as } dv = 0.$$

$$\therefore Q = (u_2 - u_1) = c_v(T_2 - T_1) \quad \dots[2.27(a)]$$

where c_v = specific heat at constant volume.

For mass, m , of working substance

$$Q = U_2 - U_1 = mc_v(T_2 - T_1) \quad \dots[2.27(b)]$$

$$[\because mu = U]$$

(2) Reversible Constant Pressure Process ($p = \text{constant}$)—*Isobaric process*

It can be seen from Fig. 2.5 (b) that when the boundary of the system is *inflexible* as in a constant volume process, then the pressure rises when heat is supplied. Hence for a constant pressure process, the boundary must move against an external resistance as heat is supplied; for instance a gas [Fig. 2.6 (a)] in a cylinder behind a piston can be made to undergo a constant pressure process. Since the *piston is pushed through a certain distance* by the force exerted by the gas, then the work is done by the gas on its surroundings.

Fig. 2.6 shows the system and states before and after the heat addition at constant pressure.

Considering unit mass of working substance and applying first law of thermodynamics to the process

$$Q = (u_2 - u_1) + W$$

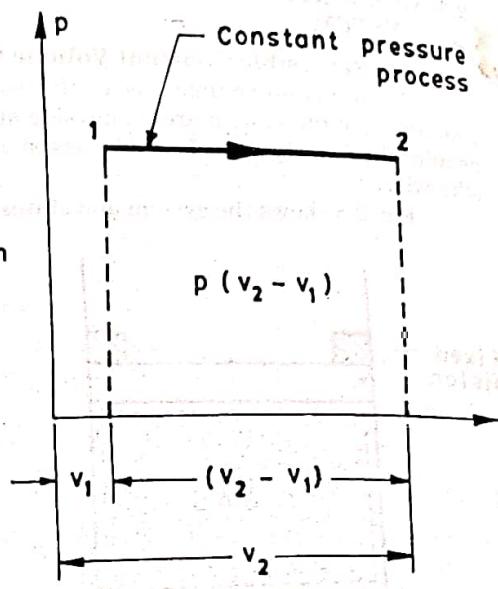
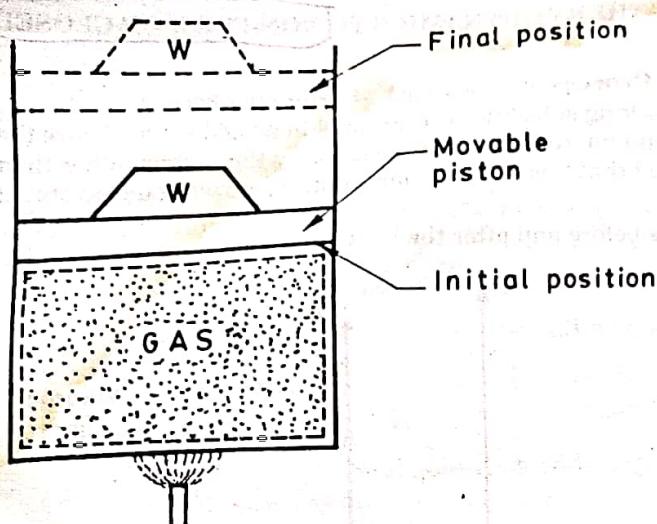


Fig. 2.6. Reversible constant pressure process.

The work done,

$$W = \int_{v_1}^{v_2} pdv = p(v_2 - v_1)$$

$$Q = (u_2 - u_1) + p(v_2 - v_1) = u_2 - u_1 + p v_2 - p v_1 \\ = (u_2 + p v_2) - (u_1 + p v_1) = h_2 - h_1$$

$$Q = h_2 - h_1 = c_p (T_2 - T_1)$$

or

where h = enthalpy (specific)

c_p = specific heat at constant pressure.

For mass, m , of working substance

$$Q = H_2 - H_1 = mc_p(T_2 - T_1)$$

[$\because h = u + pv$]

...(2.28)

(3) Reversible Temperature or Isothermal Process ($pV = \text{constant}$, $T = \text{constant}$)

(3) Reversible Temperature or Isothermal Process ($\mu_0 = \text{constant}$)

A process at a constant temperature is called an isothermal process. When a working substance in a cylinder behind a piston expands from a high pressure to a low pressure there is a tendency for the temperature to fall. In an isothermal expansion heat must be added continuously in order to keep the temperature at the initial value. Similarly in an isothermal compression heat must be removed from the working substance continuously during the process.

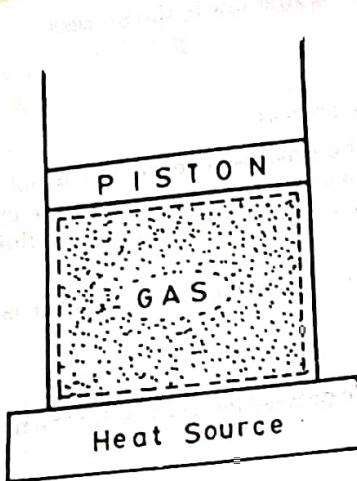
Fig. 2.7 shows the system and states before and after the heat addition at constant temperature.

Considering unit mass of working substance and applying first law to the process

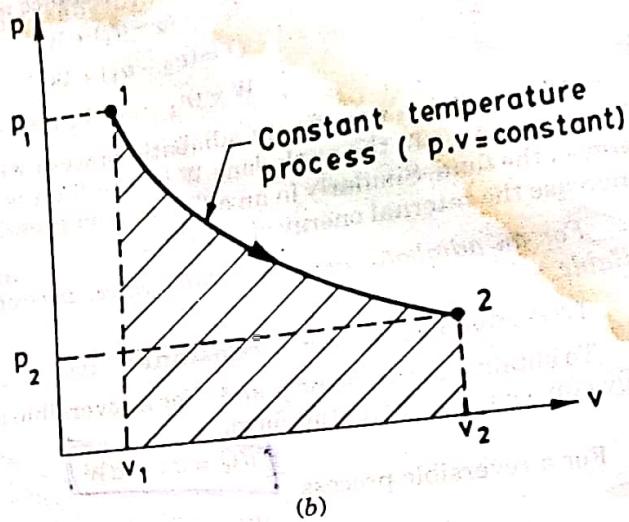
$$\begin{aligned} Q &= (u_2 - u_1) + W \\ &= c_v(T_2 - T_1) + W \\ &\approx 0 + W \quad [\because T_2 = T_1] \end{aligned}$$

CLASS

FIRST LAW OF THERMODYNAMICS



(a)



(b)

Fig. 2.7. Reversible isothermal process.

The work done,

$$W = \int_1^2 p \, dv$$

In this case $pv = \text{constant}$ or $p = \frac{C}{v}$ (where $C = \text{constant}$)

$$W = \int_{v_1}^{v_2} C \frac{dv}{v} = C \left[\log_e v \right]_{v_1}^{v_2} = C \log_e \frac{v_2}{v_1}$$

The constant C can either be written as $p_1 v_1$ or as $p_2 v_2$, since
 $p_1 v_1 = p_2 v_2 = \text{constant}$, C

$$W = p_1 v_1 \log_e \frac{v_2}{v_1} \text{ per unit mass of working substance}$$

i.e.,

$$W = p_2 v_2 \log_e \frac{v_1}{v_2} \text{ per unit mass of working substance}$$

or

$$Q = W = p_1 v_1 \log_e \frac{v_2}{v_1} \quad \dots(2.29)$$

For mass, m , of the working substance

$$Q = p_1 V_1 \log_e \frac{V_2}{V_1} \quad \dots(2.29(a))$$

or

$$Q = p_1 V_1 \log_e \frac{p_1}{p_2} \quad \left[\because \frac{V_2}{V_1} = \frac{p_1}{p_2} \right] \quad \dots(2.29(b))$$

(4) Reversible Adiabatic Process ($pv^\gamma = \text{constant}$)

An adiabatic process is one in which no heat is transferred to or from the fluid during the process. Such a process can be reversible or irreversible. The reversible adiabatic non-flow process will be considered in this section.

Considering unit mass of working substance and applying first law to the process

$$Q = (u_2 - u_1) + W$$

$$O = (u_2 - u_1) + W$$

$$W = (u_1 - u_2) \text{ for any adiabatic process}$$

...(2.30)

or

Eqn. (2.30) is true for an adiabatic process whether the process is reversible or not. In an adiabatic expansion, the work done W by the fluid is at the expense of a reduction in the internal energy of the fluid. Similarly in an adiabatic compression process all the work done on the fluid goes to increase the internal energy of the fluid.

For an adiabatic process to take place, perfect thermal insulation for the system must be available.

To derive the law $pV^\gamma = \text{constant}$:

To obtain a law relating p and V for a reversible adiabatic process let us consider the non-flow energy equation in differential form,

$$dQ = du + dW$$

For a reversible process

$$dW = pdv$$

$$\therefore dQ = du + pdv = 0$$

(Since for an adiabatic process $Q = 0$)

Also for a perfect gas

$$pV = RT \quad \text{or} \quad p = \frac{RT}{V}$$

Hence substituting,

$$du + \frac{RTdv}{V} = 0$$

Also

$$u = c_v T \quad \text{or} \quad du = c_v dT$$

$$\therefore c_v dT + \frac{RTdv}{V} = 0$$

Dividing both sides by T , we get

$$c_v \frac{dT}{T} + \frac{Rdv}{V} = 0$$

* Integrating

$$c_v \log_e T + R \log_e V = \text{constant}$$

$$\text{Substituting } T = \frac{PV}{R}$$

$$c_v \log_e \frac{PV}{R} + R \log_e V = \text{constant}$$

Dividing throughout both sides by c_v

$$\log_e \frac{PV}{R} + \frac{R}{c_v} \cdot \log_e V = \text{constant}$$

Again

$$c_v = \frac{R}{(\gamma - 1)} \quad \text{or} \quad \frac{R}{c_v} = \gamma - 1$$

Hence substituting

$$\log_e \frac{PV}{R} + (\gamma - 1) \log_e V = \text{constant}$$

FIRST LAW OF THERMODYNAMICS

$$\log_e \frac{pv}{R} + \log_e v^{\gamma-1} = \text{constant}$$

$$\log_e \frac{pv \times v^{\gamma-1}}{R} = \text{constant}$$

$$\log_e \frac{pv^\gamma}{R} = \text{constant}$$

i.e.,

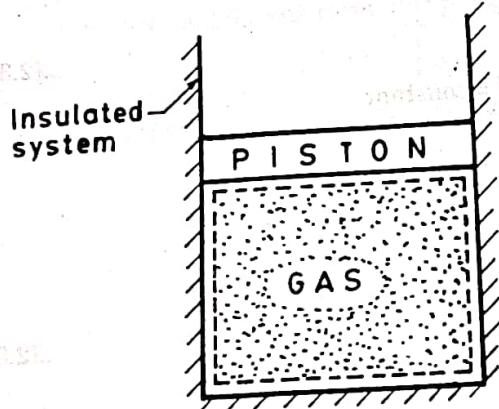
$$\frac{pv^\gamma}{R} = e^{\text{constant}} = \text{constant}$$

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

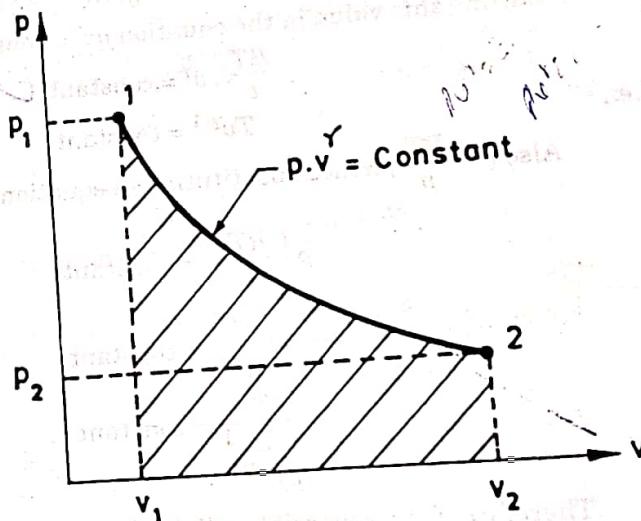
or

Expression for work W: A reversible adiabatic process for a perfect gas is shown on a p - v diagram in Fig. 2.8 (b).

A reversible adiabatic process for a perfect gas is shown on a p - v diagram in Fig. 2.8 (b).



(a)



(b)

Fig. 2.8. Reversible adiabatic process.

The work done is given by the shaded area, and this area can be evaluated by integration.

i.e.,

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

Therefore, since $pv^\gamma = \text{constant}$, C , then

$$W = \int_{v_1}^{v_2} C \frac{dv}{v^\gamma} \quad \left[\because p = \frac{C}{v^\gamma} \right]$$

i.e.,

$$W = C \int_{v_1}^{v_2} \frac{dv}{v^\gamma} = C \left| \frac{v^{-\gamma+1}}{-\gamma+1} \right|_{v_1}^{v_2}$$

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

The constant in this equation can be written as $p_1 v_1^\gamma$ or as $p_2 v_2^\gamma$. Hence,

$$W = \frac{p_1 v_1^\gamma v_1^{-\gamma+1} - p_2 v_2^\gamma v_2^{-\gamma+1}}{\gamma - 1} = \frac{p_1 v_1 - p_2 v_2}{\gamma - 1}$$

i.e.,

$$W = \frac{p_1 v_1 - p_2 v_2}{\gamma - 1}$$

or

$$W = \frac{R(T_1 - T_2)}{\gamma - 1} \quad \dots(2.32)$$

Relationship between T and v, and T and p :

By using equation $pv = RT$, the relationship between T and v , and T and p , may be derived as follows :

i.e.,

$$pv = RT$$

$$p = \frac{RT}{v}$$

Putting this value in the equation $pv^\gamma = \text{constant}$

$$\frac{RT}{v} \cdot v^\gamma = \text{constant}$$

i.e.,

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

Also $v = \frac{RT}{p}$; hence substituting in equation $pv^\gamma = \text{constant}$...(2.34)

$$p \left(\frac{RT}{p} \right)^\gamma = \text{constant}$$

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

or

$$\frac{T}{p^{\gamma-1}} = \text{constant}$$

...(2.35)

Therefore, for a reversible adiabatic process for a perfect gas between states 1 and 2, we can write :

From Eqn. (2.31),

$$p_1 v_1^\gamma = p_2 v_2^\gamma \quad \text{or} \quad \frac{p_2}{p_1} = \left(\frac{v_1}{v_2} \right)^\gamma \quad \dots(2.36)$$

From Eqn. (2.34),

$$T_1 v_1^{\gamma-1} = T_2 v_2^{\gamma-1} \quad \text{or} \quad \frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{\gamma-1} \quad \dots(2.37)$$

From Eqn. (2.35),

$$\frac{T_1}{(p_1)^\gamma} = \frac{T_2}{(p_2)^\gamma} \quad \text{or} \quad \frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{\gamma-1} \quad \dots(2.38)$$

From Eqn. (2.30), the work done in an adiabatic process per kg of gas is given by $W = (u_1 - u_2)$. The gain in internal energy of a perfect gas is given by equation :

$$u_2 - u_1 = c_v (T_2 - T_1) \quad (\text{for } 1 \text{ kg})$$

∴

$$W = c_v (T_1 - T_2)$$

FIRST LAW OF THERMODYNAMICS

Also, we know that

$$c_v = \frac{R}{\gamma - 1}$$

Hence substituting, we get

$$W = \frac{R(T_1 - T_2)}{\gamma - 1}$$

Using equation,

$$pv = RT$$

$$W = \frac{p_1v_1 - p_2v_2}{\gamma - 1}$$

This is the same expression obtained before as Eqn. (2.32).

5. Polytropic Reversible Process ($p v^n = \text{constant}$)

It is found that many processes in practice approximate to a reversible law of form $p v^n = \text{constant}$, where n is a constant. Both vapours and perfect gases obey this type of law closely in many non-flow processes. Such processes are internally reversible.

We know that for any reversible process,

$$W = \int p dv$$

For a process in $p v^n = \text{constant}$, we have

$$p = \frac{C}{v^n}, \text{ where } C \text{ is a constant}$$

$$W = C \int_{v_1}^{v_2} \frac{dv}{v^n} = C \left| \frac{v^{-n+1}}{-n+1} \right| = C \left(\frac{v_2^{-n+1} - v_1^{-n+1}}{-n+1} \right)$$

$$\therefore W = C \left(\frac{v_1^{-n+1} - v_2^{-n+1}}{n-1} \right) = \frac{p_1 v_1^n v_1^{-n+1} - p_2 v_2^n v_2^{-n+1}}{n-1}$$

i.e.,

(since the constant C , can be written as $p_1 v_1^n$ or as $p_2 v_2^n$)

$$\text{i.e., Work done, } W = \frac{p_1 v_1 - p_2 v_2}{n-1} \quad \dots(2.39)$$

$$\text{or } W = \frac{R(T_1 - T_2)}{n-1} \quad \dots(2.40)$$

Eqn. (2.39) is true for any working substance undergoing a reversible polytropic process. It follows also that for any polytropic process, we can write

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2} \right)^n \quad \dots(2.41)$$

The following relations can be derived (following the same procedure as was done under reversible adiabatic process)

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{n-1} \quad \dots(2.42)$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} \quad \dots(2.43)$$

Heat transfer during polytropic process (for perfect gas $pV = RT$):

Using non-flow energy equation, the heat flow/transfer during the process can be found,
i.e.,

$$Q = (u_2 - u_1) + W \\ = c_v(T_2 - T_1) + \frac{R(T_1 - T_2)}{n - 1}$$

i.e.,

$$Q = \frac{R(T_1 - T_2)}{n - 1} - c_v(T_1 - T_2)$$

Also

$$c_v = \frac{R}{(\gamma - 1)}$$

On substituting,

$$Q = \frac{R}{n - 1}(T_1 - T_2) - \frac{R}{(\gamma - 1)}(T_1 - T_2)$$

i.e.,

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

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

$$\therefore Q = \frac{(\gamma - n)}{(\gamma - 1)} \frac{R(T_1 - T_2)}{(n - 1)}$$

or

$$Q = \left(\frac{\gamma - n}{\gamma - 1} \right) W \quad \left[\because W = \frac{R(T_1 - T_2)}{(n - 1)} \right] \quad \dots(2.44)$$

In a polytropic process, the index n depends only on the heat and work quantities during the process. The various processes considered earlier are special cases of polytropic process for a perfect gas. For example,

When $n = 0$ $pv^0 = \text{constant}$ i.e. $p = \text{constant}$

When $n = \infty$ $pv^\infty = \text{constant}$

or $p^{1/\infty} v = \text{constant}$, i.e., $v = \text{constant}$

When $n = 1$ $pv = \text{constant}$, i.e., $T = \text{constant}$

[since $(pv)/T = \text{constant}$ for a perfect gas]

When $n = \gamma$ $pv^\gamma = \text{constant}$, i.e., reversible adiabatic

This is illustrated on a $p-v$ diagram in Fig. 2.9.

- (i) State 1 to state A is constant pressure cooling ($n = 0$).
- (ii) State 1 to state B is isothermal compression ($n = 1$).
- (iii) State 1 to state C is reversible adiabatic compression ($n = \gamma$).
- (iv) State 1 to state D is constant volume heating ($n = \infty$).

Similarly,

- (i) State 1 to state A' is constant pressure heating ($n = 0$).

- (ii) State 1 to state B' is isothermal expansion ($n = 1$).

- (iii) State 1 to state C' is reversible adiabatic expansion ($n = \gamma$).

- (iv) State 1 to state D' is constant volume cooling ($n = \infty$).

It may be noted that, since γ is always greater than unity, then process 1 to C must lie between processes 1 to B and 1 to D; similarly, process 1 to C' must lie between processes 1 to B' and 1 to D'.

CLAS

FIRST LAW OF THERMODYNAMICS

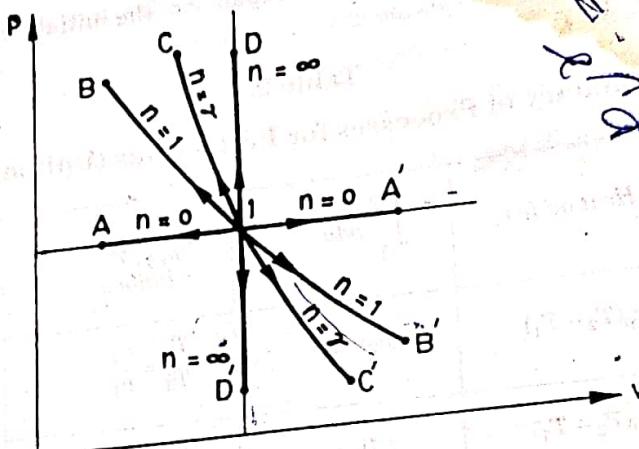


Fig. 2.9. Polytropic process.

6. Free Expansion

Consider two vessels 1 and 2 interconnected by a short pipe with a valve A, and perfectly thermally insulated [Fig. 2.10]. Initially let the vessel 1 be filled with a fluid at a certain pressure, and let 2 be completely evacuated. When the valve A is opened the fluid in 1 will expand rapidly to fill both vessels 1 and 2. The pressure finally will be lower than the initial pressure in vessel 1. This is known as *free or unresisted expansion*. The process is *highly irreversible*; since the fluid is eddying continuously during the process. Now applying first law of thermodynamics (or non-flow energy equation) between the initial and final states,

$$Q = (u_2 - u_1) + W$$

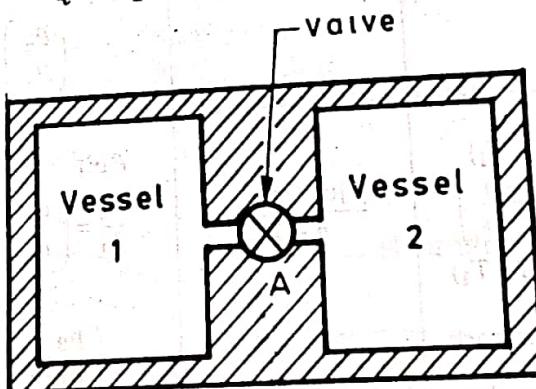


Fig. 2.10. Free expansion.

In this process, no work is done on or by the fluid, since the boundary of the system does not move. No heat flows to or from the fluid since the system is well lagged. The process is therefore, *adiabatic but irreversible*.

i.e.,

$$u_2 - u_1 = 0 \quad \text{or} \quad u_2 = u_1$$

In a free expansion, therefore, the internal energy initially equals the initial energy finally.

For a perfect gas,

$$u = c_v T$$

∴ For a free expansion of a perfect gas,

$$c_v T_1 = c_v T_2$$

$$\text{i.e.,} \quad T_1 = T_2$$

That is, for a perfect gas undergoing a free expansion, the initial temperature is equal to the final temperature.

Table 2.1
Summary of Processes for Perfect Gas (Unit mass)

Process	Index n	Heat added	$\int_1^2 pdv$	p, v, T relations	Specific heat, c
Constant pressure	$n = 0$	$c_p(T_2 - T_1)$	$p(v_2 - v_1)$	$\frac{T_2}{T_1} = \frac{v_2}{v_1}$	c_p
Constant volume	$n = \infty$	$c_v(T_2 - T_1)$	0	$\frac{T_1}{T_2} = \frac{p_1}{p_2}$	c_v
Constant temperature	$n = 1$	$p_1 v_1 \log_e \frac{v_2}{v_1}$	$p_1 v_1 \log_e \frac{v_2}{v_1}$	$p_1 v_1 = p_2 v_2$	∞
Reversible adiabatic	$n = \gamma$	0	$\frac{p_1 v_1 - p_2 v_2}{\gamma - 1}$	$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{\gamma-1}$ $= \left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}}$	0
Polytropic	$n = n$	$c_n(T_2 - T_1)$ $= c_v \left(\frac{\gamma - n}{1 - n} \right) \times (T_2 - T_1)$ $= \frac{\gamma - n}{\gamma - 1} \times \text{work done (non-flow)}$	$\frac{p_1 v_1 - p_2 v_2}{n - 1}$	$p_1 v_1^n = p_2 v_2^n$ $\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{n-1}$ $= \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}}$	$c_n = c_v \left(\frac{\gamma - n}{1 - n} \right)$

Note. Equations must be used keeping dimensional consistence.

✓ **Example 2.1.** In an internal combustion engine, during the compression stroke the heat rejected to the cooling water is 50 kJ/kg and the work input is 100 kJ/kg.

Calculate the change in internal energy of the working fluid stating whether it is a gain or loss.

Solution. Heat rejected to the cooling water, $Q = -50 \text{ kJ/kg}$
(-ve sign since heat is rejected)

Work input, $W = -100 \text{ kJ/kg}$

(-ve sign since work is supplied to the system)

CLASSE

FIRST LAW OF THERMODYNAMICS

Using the relation,

$$\begin{aligned} Q &= (u_2 - u_1) + W \\ -50 &= (u_2 - u_1) - 100 \\ u_2 - u_1 &= -50 + 100 = 50 \text{ kJ/kg} \end{aligned}$$

or

Hence, gain in internal energy = 50 kJ/kg. (Ans.)

Example 2.2. In an air motor cylinder the compressed air has an internal energy of 450 kJ/kg at the beginning of the expansion and an internal energy of 220 kJ/kg after expansion. If the work done by the air during the expansion is 120 kJ/kg, calculate the heat flow to and from the cylinder.

Solution. Internal energy at beginning of the expansion,

$$u_1 = 450 \text{ kJ/kg}$$

Internal energy after expansion,

$$u_2 = 220 \text{ kJ/kg}$$

Work done by the air during expansion,

$$W = 120 \text{ kJ/kg}$$

Heat flow, Q:

Using the relation,

$$Q = (u_2 - u_1) + W$$

$$Q = (220 - 450) + 120$$

$$\therefore -230 + 120 = -110 \text{ kJ/kg}$$

Hence, heat rejected by air = 110 kJ/kg. (Ans.)

Example 2.3. 0.3 kg of nitrogen gas at 100 kPa and 40°C is contained in a cylinder. The piston is moved compressing nitrogen until the pressure becomes 1 MPa and temperature becomes 160°C. The work done during the process is 30 kJ.

Calculate the heat transferred from the nitrogen to the surroundings.

$$c_v \text{ for nitrogen} = 0.75 \text{ kJ/kg K}$$

Solution. Mass of nitrogen, $m = 0.3 \text{ kg}$

Temperature before compression = 40°C or 313 K

Temperature after compression = 160°C or 433 K

The work done during the compression process, $W = -30 \text{ kJ}$

According to first law of thermodynamics,

$$Q = \Delta U + W = (U_2 - U_1) + W$$

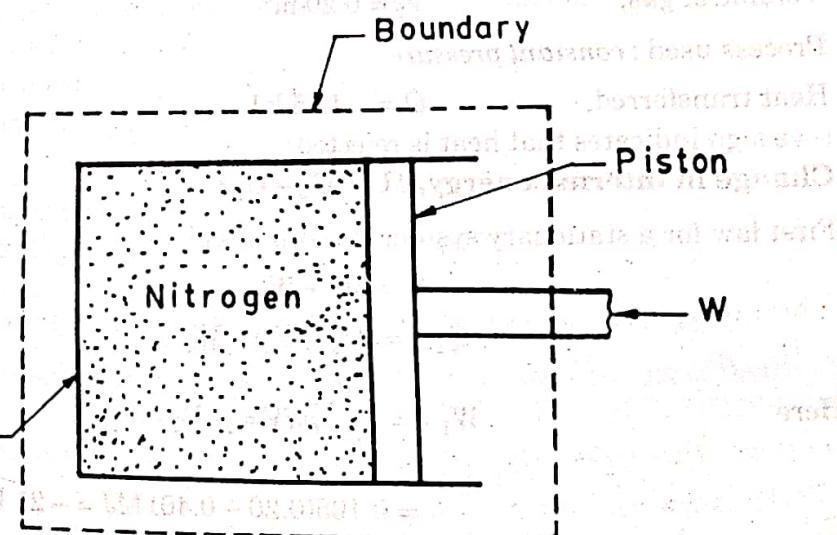


Fig. 2.11

FIRST LAW OF THERMODYNAMICS

Substituting this value of W_{1-2} in equation (i), we get
 $-42.5 = (U_2 - U_1) - 21$
 $U_2 - U_1 = -42.5 + 21 = -21.5 \text{ kJ}$

Hence 'decrease' in internal energy = 21.5 kJ. (Ans.)

✓ Example 2.5. A container is divided into compartments by a partition. The container is completely insulated so that there is no heat transfer. One portion contains gas at temperature T_1 and pressure p_1 while the other portion also has the same gas but at temperature T_2 and pressure p_2 . How will the First Law of Thermodynamics conclude the result if partition is removed?

Solution. Refer Fig. 2.13.

According to First Law of Thermodynamics,

$$\delta Q = \delta U + \delta W$$

When partition removed, $\delta Q = 0$

$$\delta W = 0$$

$$\delta U = 0.$$

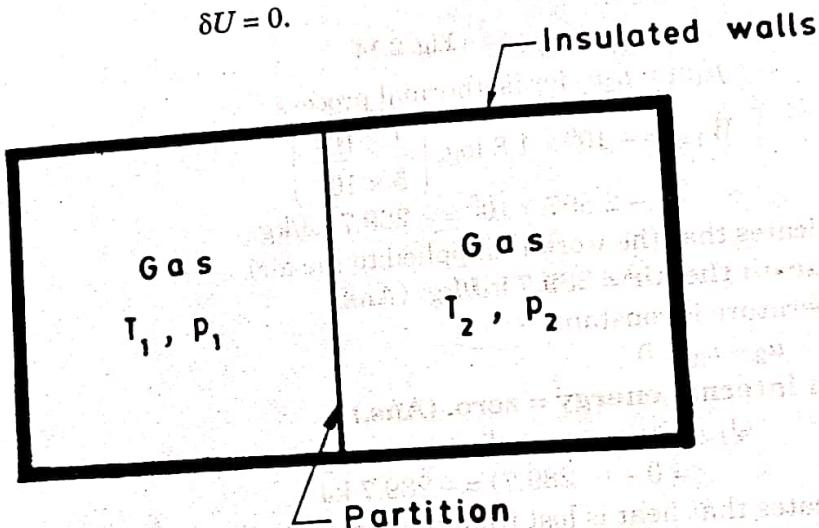


Fig. 2.13

Conclusion. There is conservation of internal energy.

✓ Example 2.6. Air enters a compressor at 10^5 Pa and 25°C having volume of $1.8 \text{ m}^3/\text{kg}$ and is compressed to $5 \times 10^5 \text{ Pa}$ isothermally.

Determine : (i) Work done ;

(ii) Change in internal energy ; and

(iii) Heat transferred.

Solution. Initial pressure of air, $p_1 = 10^5 \text{ Pa}$

Initial temperature of air, $T_1 = 25 + 273 = 298 \text{ K}$

Final pressure of air, $p_2 = 5 \times 10^5 \text{ Pa}$

Final temperature of air, $T_2 = T_1 = 298 \text{ K}$ (isothermal process)

Since, it is a closed steady state process, we can write down the first law of thermodynamics as,

$$Q = (u_2 - u_1) + W \dots \text{per kg}$$

(i) For isothermal process :

$$W_{1-2} = \int_1^2 p \cdot dv = p_1 v_1 \log_e \left(\frac{p_1}{p_2} \right)$$

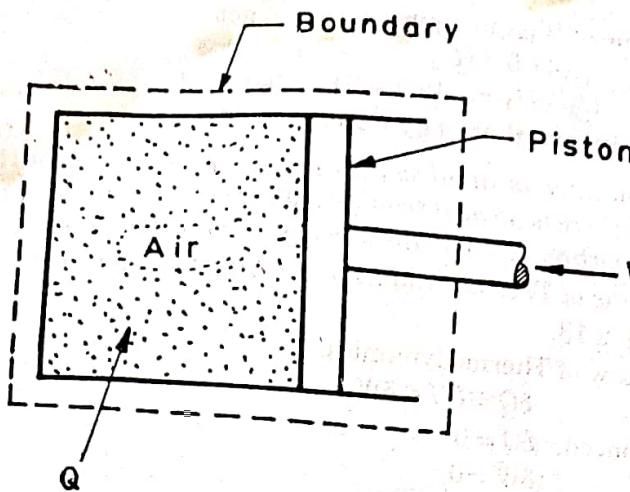


Fig. 2.14

as

$$p_1 v_1 = p_2 v_2 \text{ for isothermal process}$$

$$\therefore W_{1-2} = -10^5 \times 1.8 \log_e \left(\frac{1 \times 10^5}{5 \times 10^5} \right) \\ = -2.897 \times 10^5 = -289.7 \text{ kJ/kg.}$$

(-ve sign indicates that the work is supplied to the air)

\therefore Work done on the air = 289.7 kJ/kg. (Ans.)

(ii) Since temperature is constant,

$$\therefore u_2 - u_1 = 0$$

\therefore Change in internal energy = zero. (Ans.)

(iii) Again,

$$Q_{1-2} = (u_2 - u_1) + W$$

$$= 0 + (-289.7) = -289.7 \text{ kJ}$$

(-ve sign indicates that heat is lost from the system to the surroundings)

\therefore Heat rejected = 289.7 kJ/kg. (Ans.)

Example 2.7. A cylinder containing the air comprises the system. Cycle is completed as follows :

(i) 82000 N-m of work is done by the piston on the air during compression stroke and 45 kJ of heat are rejected to the surroundings.

(ii) During expansion stroke 100000 N-m of work is done by the air on the piston. Calculate the quantity of heat added to the system.

Solution. Refer Fig. 2.15.

Compression stroke. Process 1-2 :

Work done by the piston on the air, $W_{1-2} = -82000 \text{ N-m} (= -82 \text{ kJ})$

Heat rejected to the system, $Q_{1-2} = -45 \text{ kJ}$

Now,

$$Q_{1-2} = (U_2 - U_1) + W$$

$$-45 = (U_2 - U_1) + (-82)$$

$$(U_2 - U_1) = 37 \text{ kJ}$$

Expansion stroke. Process 2-1 : ... (i)

Work done by air on the piston, $W_{2-1} = 100000 \text{ N-m} (= 100 \text{ kJ})$

Now,

$$Q_{2-1} = (U_1 - U_2) + W$$

$$= -37 + 100 \text{ kJ} = 63 \text{ kJ}$$

Hence, quantity of heat added to the system = 63 kJ. (Ans.)

FIRST LAW OF THERMODYNAMICS

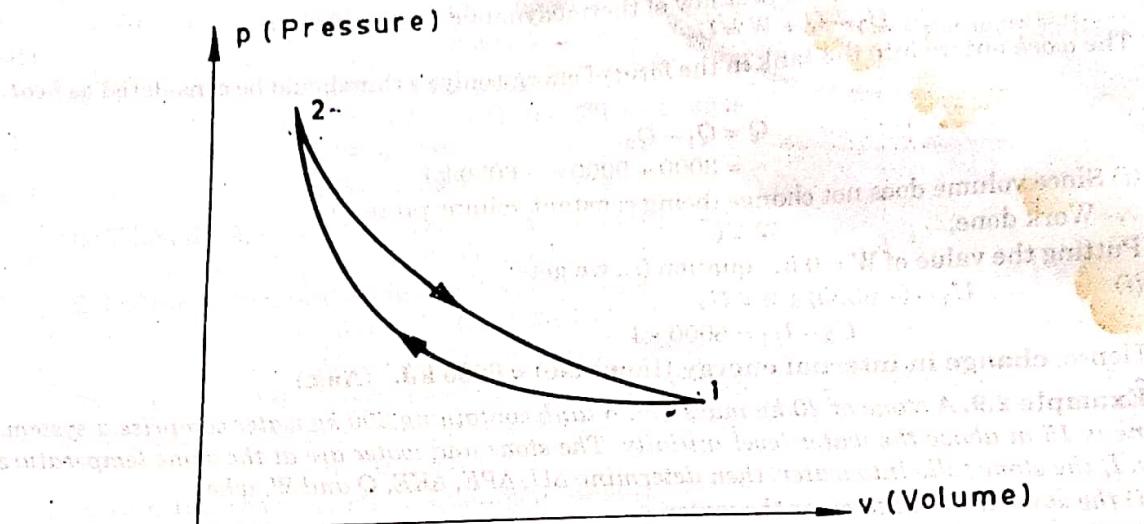


Fig. 2.15

Example 2.8. A tank containing air is stirred by a paddle wheel. The work input to the paddle wheel is 9000 kJ and the heat transferred to the surroundings from the tank is 3000 kJ.

Determine : (i) Work done ; (by Taylor eqn)

(ii) Change in internal energy of the system.

Solution. Refer Fig. 2.16.

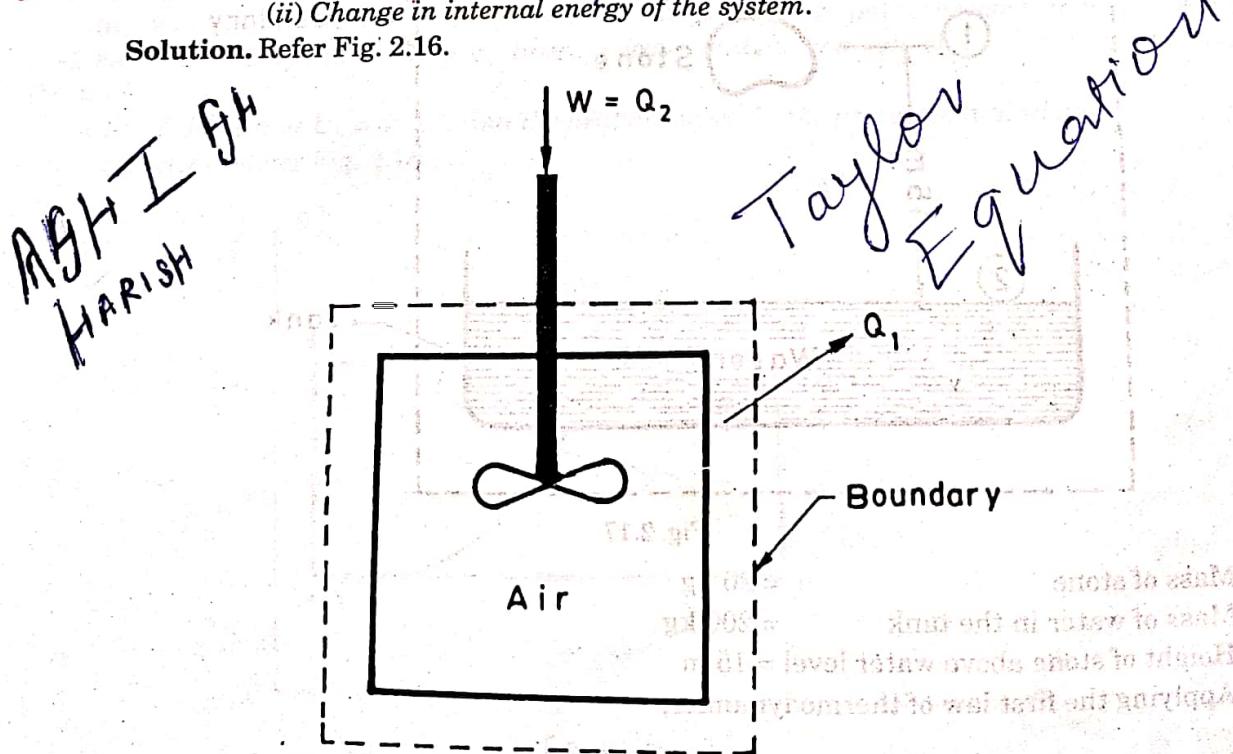


Fig. 2.16

Work input to the paddle wheel = 9000 kJ

Heat transferred to the surroundings from the tank = 3000 kJ

As it is a closed system, the first law of thermodynamics can be written as

$$U_1 = Q + W = U_2$$

The work enters into the tank in the form of energy only so this should be considered as heat input. ... (i)

$$\therefore Q = Q_1 - Q_2$$

$$= 3000 - 9000 = - 6000 \text{ kJ.}$$

(i) Since volume does not change (being constant volume process)

$$\therefore \text{Work done, } W = 0$$

Putting the value of $W = 0$ in equation (i), we get

$$(ii) U_1 - (- 6000) + 0 = U_2$$

$$\therefore U_2 - U_1 = 6000 \text{ kJ}$$

Hence, change in internal energy (increase) = 6000 kJ. (Ans.)

Example 2.9. A stone of 20 kg mass and a tank containing 200 kg water comprise a system. The stone is 15 m above the water level initially. The stone and water are at the same temperature initially. If the stone falls into water, then determine ΔU , ΔPE , ΔKE , Q and W , when

(i) the stone is about to enter the water,

(ii) the stone has come to rest in the tank, and

(iii) the heat is transferred to the surroundings in such an amount that the stone and water come to their initial temperature.

Solution. Refer Fig. 2.17.

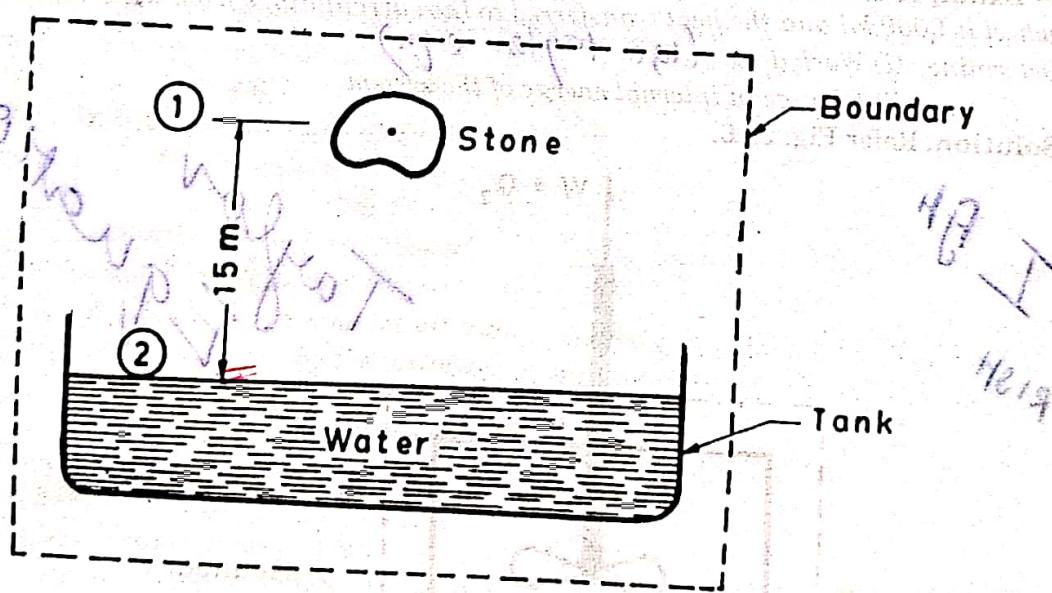


Fig. 2.17

Mass of stone

$$\approx 20 \text{ kg}$$

Mass of water in the tank

$$= 200 \text{ kg}$$

Height of stone above water level = 15 m

Applying the first law of thermodynamics,

$$\begin{aligned} Q &= (U_2 - U_1) + m \left[\frac{C_2^2 - C_1^2}{2} \right] + mg(Z_2 - Z_1) + W \\ &= \Delta U + \Delta KE + \Delta PE + W \end{aligned}$$

Here

Q = heat leaving the boundary.

CLASSE

FIRST LAW OF THERMODYNAMICS

(i) When the stone is about to enter the water,
 $Q = 0, W = 0, \Delta U = 0$

$$\begin{aligned} -\Delta KE &= \Delta PE = mg(Z_2 - Z_1) \\ &= 20 \times 9.81 (0 - 15) = -2943 \text{ J} \\ \therefore \Delta KE &= 2943 \text{ J} \\ \Delta PE &= -2943 \text{ J. (Ans.)} \end{aligned}$$

and

(ii) When the stone dips into the tank and comes to rest
 $Q = 0, W = 0, \Delta KE = 0$

Substituting these values in equation (i), we get

$$\begin{aligned} 0 &= \Delta U + 0 + \Delta PE + 0 \\ \Delta U &= -\Delta PE = -(-2943) = 2943 \text{ J. (Ans.)} \end{aligned}$$

\therefore This shows that the internal energy (temperature) of the system increases.

(iii) When the water and stone come to their initial temperature,
 $W = 0, \Delta KE = 0$

Substituting these values in equation (i), we get
 $\therefore Q = -\Delta U = -2943 \text{ J. (Ans.)}$

The negative sign shows that the heat is lost from the system to the surroundings.

~~Example 2.10.~~ When a system is taken from state l to state m, in Fig. 2.18, along path lqm, 168 kJ of heat flows into the system, and the system does 64 kJ of work :

(i) How much will be the heat that flows into the system along path lnm if the work done is 21 kJ? (25%)

(ii) When the system is returned from m to l along the curved path, the work done on the system is 42 kJ. Does the system absorb or liberate heat, and how much of the heat is absorbed or liberated?

(iii) If $U_l = 0$ and $U_n = 84 \text{ kJ}$, find the heat absorbed in the processes ln and nm.

Solution. Refer Fig. 2.18.

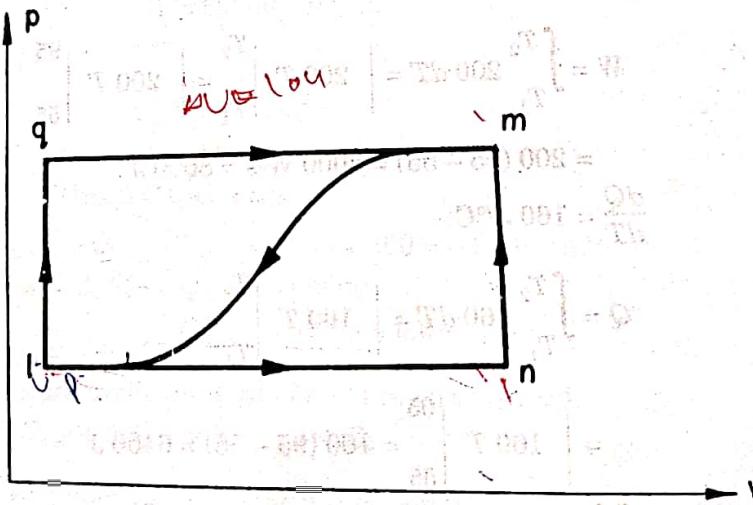


Fig. 2.18

$$Q_{l-q-m} = 168 \text{ kJ}$$

$$W_{l-q-m} = 64 \text{ kJ}$$

We have,

$$Q_{l-q-m} = (U_m - U_l) + W_{l-q-m}$$

$$\therefore \quad (i) \quad 168 = (U_m - U_l) + 64 \\ U_m - U_l = 104 \text{ kJ. (Ans.)}$$

$$\begin{aligned} Q_{l-n-m} &= (U_m - U_l) + W_{l-n-m} \\ &= 104 + 21 = 125 \text{ kJ. (Ans.)} \\ (ii) \quad Q_{m-l} &= (U_l - U_m) + W_{m-l} \\ &= -104 + (-42) = -146 \text{ kJ. (Ans.)} \end{aligned}$$

The system liberates 146 kJ.

$$(iii) \quad W_{l-n-m} = W_{l-n} + W_{n-m} = W_{l-m} = 21 \text{ kJ}$$

$$\therefore \quad Q_{l-n} = (U_n - U_l) + W_{l-n} \quad [\because W_{n-m} = 0, \text{ since volume does not change.}]$$

$$\begin{aligned} \text{Now} \quad Q_{l-n} &= 84 + 21 = 105 \text{ kJ. (Ans.)} \\ \therefore \quad Q_{l-n-m} &= 125 \text{ kJ} = Q_{l-n} + Q_{n-m} \\ Q_{n-m} &= 125 - 105 = 20 \text{ kJ. (Ans.)} \end{aligned}$$

Example 2.11. In a system, executing a non-flow process, the work and heat per degree change of temperature are given by

$$\frac{dW}{dT} = 200 \text{ W-s/C} \quad \text{and} \quad \frac{dQ}{dT} = 160 \text{ J/C}$$

What will be the change of internal energy of the system when its temperature changes from $T_1 = 55^\circ\text{C}$ to $T_2 = 95^\circ\text{C}$?

Solution. Initial temperature, $T_1 = 55^\circ\text{C}$; Final temperature, $T_2 = 95^\circ\text{C}$

$$\frac{dW}{dT} = 200 \text{ W-s/C} ; \quad \frac{dQ}{dT} = 160 \text{ J/C.}$$

Change of internal energy:

Now,

$$\frac{dW}{dT} = 200 \text{ W-s/C}$$

∴

$$W = \int_{T_1}^{T_2} 200 dT = \left| 200 T \right|_{T_1}^{T_2} = \left| 200 T \right|_{55}^{95}$$

$$= 200 (95 - 55) = 8000 \text{ W-s} = 8000 \text{ J}$$

Also,

$$\frac{dQ}{dT} = 160 \text{ J/C} \quad [\because 1 \text{ W-s} = 1 \text{ J}]$$

∴

$$\begin{aligned} Q &= \int_{T_1}^{T_2} 160 dT = \left| 160 T \right|_{T_1}^{T_2} \\ &= \left| 160 T \right|_{55}^{95} = 160 (95 - 55) = 6400 \text{ J} \end{aligned}$$

Applying the first law of thermodynamics to the given non-flow system,

$$Q = \Delta U + W$$

$$6400 = \Delta U + 8000$$

$$\Delta U = -1600 \text{ J} = -1.6 \text{ kJ. (Ans.)}$$

or

The -ve sign indicates that there is decrease in internal energy.

Date _____
Page _____

FIRST LAW OF THERMODYNAMICS

Example 2.12. A fluid system, contained in a piston and cylinder machine, passes through a complete cycle of four processes. The sum of all heat transferred during a cycle is -340 kJ . The system completes 200 cycles per min.

Complete the following table showing the method for each item, and compute the net rate of work output in kW.

Process	$Q \text{ (kJ/min)}$	$W \text{ (kJ/min)}$	$\Delta E \text{ (kJ/min)}$
1-2	0	4340	-4340
2-3	42000	0	42000
3-4	-4200	69000	-73200
4-1	-105800	0	35540

Solution. Sum of all heat transferred during the cycle = -340 kJ .

Number of cycles completed by the system = 200 cycles/min.

Process 1-2 :

$$Q = \Delta E + W$$

$$0 = \Delta E + 4340$$

$$\therefore \Delta E = -4340 \text{ kJ/min.}$$

Process 2-3 :

$$Q = \Delta E + W$$

$$42000 = \Delta E + 0$$

$$\Delta E = 42000 \text{ kJ/min.}$$

Process 3-4 :

$$Q = \Delta E + W$$

$$-4200 = -73200 + W$$

$$\therefore W = 69000 \text{ kJ/min.}$$

Process 4-1 :

$$\sum Q = -340 \text{ kJ}$$

cycle

The system completes 200 cycles/min

$$\therefore Q_{1-2} + Q_{2-3} + Q_{3-4} + Q_{4-1} = -340 \times 200 = -68000 \text{ kJ/min}$$

or

$$0 + 42000 + (-4200) + Q_{4-1} = -68000$$

$$Q_{4-1} = -105800 \text{ kJ/min.}$$

Now, $\int dE = 0$, since cyclic integral of any property is zero.

$$\Delta E_{1-2} + \Delta E_{2-3} + \Delta E_{3-4} + \Delta E_{4-1} = 0$$

$$-4340 + 42000 + (-73200) + \Delta E_{4-1} = 0$$

$$\therefore \Delta E_{4-1} = 35540 \text{ kJ/min.}$$

∴

$$W_{4-1} = Q_{4-1} - \Delta E_{4-1}$$

$$= -105800 - 35540 = -141340 \text{ kJ/min}$$

The completed table is given below:

Process	$Q(kJ/min)$	$W(kJ/min)$	$\Delta E(kJ/min)$
1-2	0	4340	
2-3	42000	0	-4340
3-4	-4200	69000	42000
4-1	-105800	-141340	-73200
Since			35540

Rate of work output

$$\sum Q_{\text{cycle}} = \sum W_{\text{cycle}}$$

$$= -68000 \text{ kJ/min} = -\frac{68000}{60} \text{ kJ/s or kW}$$

$$= 1133.33 \text{ kW. (Ans.)}$$

Example 2.13. The power developed by a turbine in a certain steam plant is 1200 kW. The heat supplied to the steam in the boiler is 3360 kJ/kg, the heat rejected by the system to cooling water in the condenser is 2520 kJ/kg and the feed pump work required to pump the condensate back into the boiler is 6 kW.

Calculate the steam flow round the cycle in kg/s.

Solution. The power developed by a turbine = 1200 kW

The heat supplied to the steam in the boiler = 3360 kJ/kg

The heat rejected by the system to cooling water = 2520 kJ/kg

Feed pump work = 6 kW

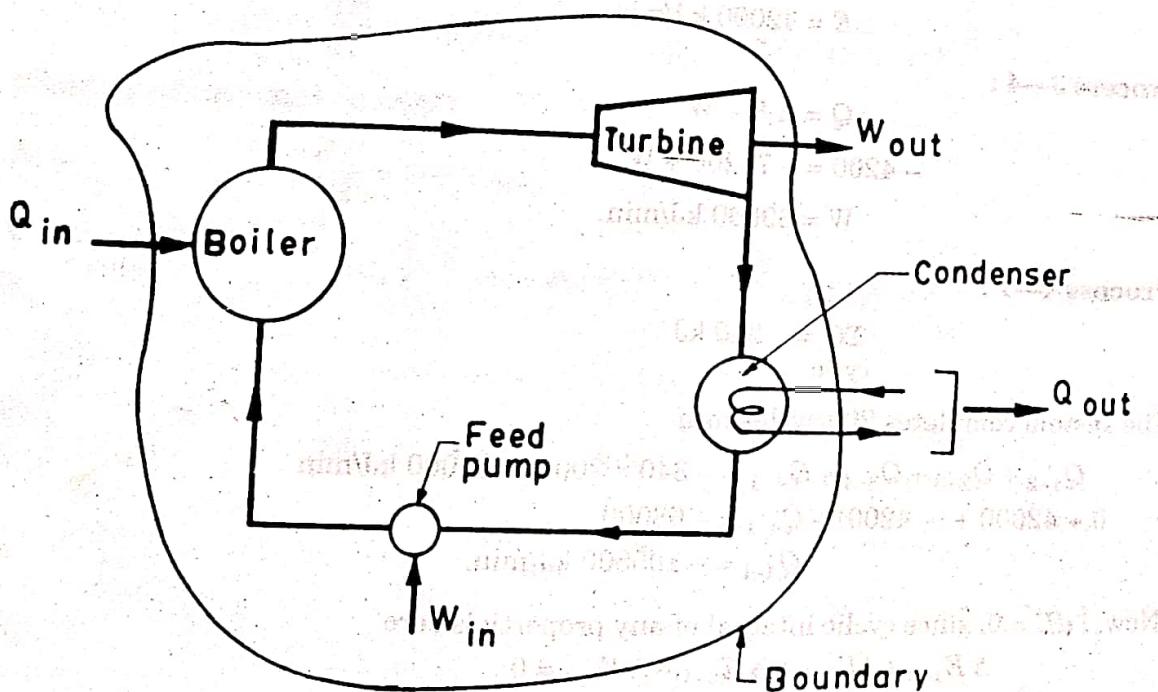


Fig. 2.19

Fig. 2.19 shows the cycle. A boundary is shown which encompasses the entire plant. Strictly, this boundary should be thought of as encompassing the working fluid only.

$$\oint dQ = 3360 - 2520 = 840 \text{ kJ/kg}$$

✓

FIRST LAW OF THERMODYNAMICS

Let the system flow be in kg/s.

$$\oint dQ = 840 \dot{m} \text{ kJ/s}$$

$$\oint dW = 1200 - 6 = 1194 \text{ kJ/s}$$

But

$$\text{i.e., } 840 \dot{m} = 1194$$

$$\therefore \dot{m} = \frac{1194}{840} = 1.421 \text{ kg/s}$$

∴ Steam flow round the cycle = 1.421 kg/s. (Ans.)

Example 2.14. A closed system of constant volume experiences a temperature rise of 25°C when a certain process occurs. The heat transferred in the process is 30 kJ. The specific heat at constant volume for the pure substance comprising the system is $1.2 \text{ kJ/kg } ^\circ\text{C}$, and the system contains 2.5 kg of this substance. Determine :

(i) The change in internal energy ;

(ii) The work done.

Solution. Temperature rise, $(T_2 - T_1) = 25^\circ\text{C}$

The heat transferred in the process, $Q = 30 \text{ kJ}$

Specific heat at constant volume, $c_v = 1.2 \text{ kJ/kg } ^\circ\text{C}$

Mass of the substance, $m = 2.5 \text{ kg}$

$$\text{Now, } \Delta U = m \int_{T_1}^{T_2} c_v dT$$

$$= 2.5 \int_{T_1}^{T_2} 1.2 dT = 3.0 \times (T_2 - T_1)$$

$$= 3.0 \times 25 = 75 \text{ kJ}$$

Hence, the change in internal energy is 75 kJ. (Ans.)

According to the first law of thermodynamics,

$$Q = \Delta U + W$$

$$\therefore 30 = 75 + W$$

$$\therefore W = 30 - 75 = -45 \text{ kJ}$$

Hence, the work done = -45 kJ. (Ans.)

It may be observed that even though the volume is constant the work is not zero. Clearly, the process is irreversible.

Example 2.15. A system receives 50 kJ of heat while expanding with volume change of 0.14 m^3 against an atmosphere of $1.2 \times 10^5 \text{ N/m}^2$. A mass of 90 kg in the surroundings is also lifted a distance of 5.5 meters.

(i) Find the change in energy of the system.

(ii) The system is returned to its initial volume by an adiabatic process which requires 110 kJ of work. Find the change in energy of the system.

(iii) For the combined processes of (i) and (ii) determine the change in energy of the system.

Solution. Heat received by the system,

$$\text{Change in volume } Q = 50 \text{ kJ}$$

$$\Delta V = 0.14 \text{ m}^3$$

C = velocity of fluid ; Z = height above datum ; p = pressure of the fluid ; u = internal energy per kg of fluid ; pv = energy required for 1 kg of fluid.

This equation is applicable to any medium in any steady flow. It is applicable not only to rotary machines such as centrifugal fans, pumps and compressors but also to reciprocating machines such as steam engines.

In a steady flow the rate of mass flow of fluid at any section is the same as at any other section. Consider any section of cross-sectional area A , where the fluid velocity is C , the rate of volume flow past the section is CA . Also, since mass flow is volume flow divided by specific volume.

$$\text{Mass flow rate, } \dot{m} = \frac{CA}{v}$$

(where v = specific volume at the section)

This equation is known as the **continuity of mass equation**.
With reference to Fig. 2.27.

$$\therefore \dot{m} = \frac{C_1 A_1}{v_1} = \frac{C_2 A_2}{v_2}$$

...(2.46)

...[2.46 (a)]

2.11. ENERGY RELATIONS FOR FLOW PROCESS

The energy equation (m kg of fluid) for a steady flow system is given as follows :

$$m \left(u_1 + \frac{C_1^2}{2} + Z_1 g + p_1 v_1 \right) + Q = m \left(u_2 + \frac{C_2^2}{2} + Z_2 g + p_2 v_2 \right) + W$$

i.e. $Q = m \left[(u_2 - u_1) + (Z_2 g - Z_1 g) + \left(\frac{C_2^2}{2} - \frac{C_1^2}{2} \right) + (p_2 v_2 - p_1 v_1) \right] + W$

i.e., $Q = m \left[(u_2 - u_1) + g(Z_2 - Z_1) + \left(\frac{C_2^2 - C_1^2}{2} \right) + (p_2 v_2 - p_1 v_1) \right] + W$

$= \Delta U + \Delta P E + \Delta K E + \Delta(pv) + W$

where $\Delta U = m(u_2 - u_1)$

$$\Delta P E = mg(Z_2 - Z_1)$$

$$\Delta K E = m \left(\frac{C_2^2 - C_1^2}{2} \right)$$

$$\Delta pv = m(p_2 v_2 - p_1 v_1)$$

$$\therefore Q - \Delta U = [\Delta P E + \Delta K E + \Delta(pv) + W] \quad \dots(2.47)$$

For non-flow process,

$$Q = \Delta U + W = \Delta U + \int_1^2 p dV$$

$$Q - \Delta U = \int_1^2 p dV$$

...(2.48)

i.e.,

✓

FIRST LAW OF THERMODYNAMICS

The internal energy is a function of temperature only and it is a point function. Therefore, for the same two temperatures, change in internal energy is the same whatever may be the process, non-flow, or steady flow, reversible or irreversible.

For the same value of Q transferred to non-flow and steady flow process and for the same temperature range, we can equate the values of Eqns. (2.47) and (2.48) for $(Q - \Delta U)$.

$$\therefore \int_1^2 p \cdot dV = \Delta PE + \Delta KE + \Delta(pV) + W \quad \dots(2.49)$$

where W = work transfer in flow process

and $\int_1^2 p \cdot dV$ = total change in mechanical energy of reversible steady flow process.

✓ **Property Relations for Energy Equations**

We know that

$$h = u + pv$$

Differentiating above equation

$$dh = du + pdv + vdp$$

But $dQ = du + p.dv$ (as per first law applied to closed system)

or

$$du = dQ - p.dv$$

Substituting this value of du in the above equation, we get

$$dh = dQ - p.dv + pdv + vdp$$

$$= dQ + vdp$$

$$\therefore vdp = dh - dQ$$

$$\therefore - \int_1^2 vdp = Q - \Delta h$$

... (2.50)

where $- \int_1^2 vdp$ represents on a $p-v$ diagram the area behind 1-2 as shown in Fig. 2.28 (b).

The Eqn. (2.47) for a unit mass flow can be written as

$$dQ = d(PE) + d(KE) + du + d(pv) + dW$$

Substituting the value of $dQ = du + p.dv$ in the above equation, we get

$$du + pdv = d(PE) + d(KE) + du + pdv + vdp + dW$$

$$\therefore - vdp = d(PE) + d(KE) + dW$$

$$\therefore - \int_1^2 vdp = \Delta PE + \Delta KE + W$$

... [2.50 (a)]

If $\Delta PE = 0$ (as in most of thermodynamic systems)

$$- \int_1^2 vdp = \Delta KE + W$$

... [2.50 (b)]

If $W = 0$, the area behind the curve represents ΔKE and if $\Delta KE = 0$, area behind the curve represents W which is shaft work.

$- \int_1^2 vdp$ is a positive quantity and represents work done by the system.

CLASSMATE
Date _____
Page _____

FIRST LAW OF THERMODYNAMICS

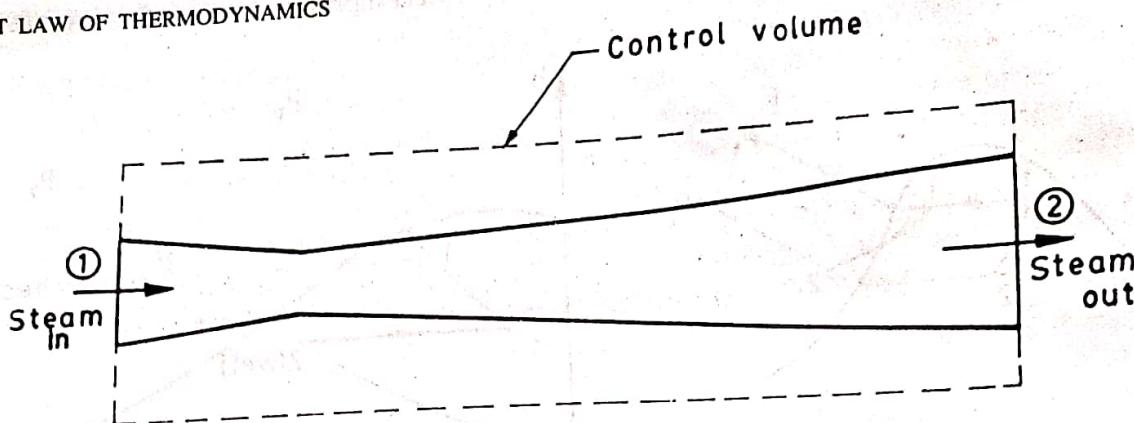


Fig. 2.68

As the enthalpy and pressure of steam at the exit of the nozzle are known, we can find out quality of steam,

$$h_g_2 \text{ (at 1.5 bar)} = 2693.4 \text{ kJ/kg}$$

As $h_2 < h_g_2$, the steam is wet.

The enthalpy of wet steam is given by

$$h_2 = h_f_2 + x_2 h_{fg_2}$$

$$2618.45 = 467.1 + x_2 \times 2226.2$$

$$x_2 = \frac{2618.45 - 467.1}{2226.2} = 0.966.$$

Hence the condition of steam leaving the nozzle is 96.6% dry. (Ans.)

6. Throttling. A flow of fluid is said to be throttled when there is some *restriction to the flow*, when the velocities before and after the restriction are either equal or negligibly small, and when there is a *negligible heat loss to the surroundings*.

The restriction to the flow can be :

- (i) partly open valve
- (ii) an orifice or
- (iii) any other sudden reduction in the cross-section of the flow.

An example of throttling is shown in Fig. 2.69. It is represented on *T-s* and *h-s* diagrams as shown in Fig. 2.70 and 2.71 respectively. The fluid (say steam) flowing steadily along a well-lagged pipe, passes through an orifice at section X. Since the pipe is well-lagged it can be assumed that no heat flows to or from the fluid.

Applying flow equation between any two sections of the flow, we have

$$h_1 + \frac{C_1^2}{2} + Q = h_2 + \frac{C_2^2}{2} + W$$

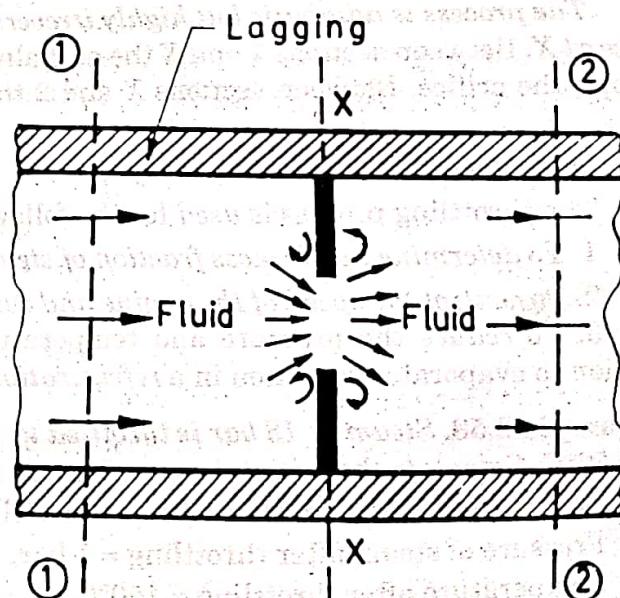


Fig. 2.69. Throttling.

Second Law of Thermodynamics and Entropy

- 3.1. Limitations of first law of thermodynamics and introduction to second law. 3.2. Performance of heat engine and reversible heat engine. 3.3. Reversible processes. 3.4. Statements of second law of thermodynamics—Clausius statement—Kelvin-Planck statement—Equivalence of Clausius statement to the Kelvin-Planck statement. 3.5. Perpetual motion machine of the second kind. 3.6. Thermodynamic temperature. 3.7. Clausius inequality. 3.8. Carnot cycle. 3.9. Carnot's theorem. 3.10. Corollary of Carnot's theorem. 3.11. Efficiency of the reversible heat engine. 3.12. Entropy—Introduction—a property of a system—Change of entropy in a reversible process. 3.13. Entropy and irreversibility. 3.14. Change in entropy of the universe. 3.15. Temperature entropy diagram. 3.16. Characteristics of entropy. 3.17. Entropy changes for a closed system—General case for change of entropy of a gas—Heating a gas at constant volume—Heating a gas at constant pressure—Isothermal process—Adiabatic process—Polytropic process—Approximation for heat absorbed. 3.18. Entropy changes for an open system—Highlights—Objective Type Questions—Theoretical Questions—Unsolved Examples.

3.1. LIMITATIONS OF FIRST LAW OF THERMODYNAMICS AND INTRODUCTION TO SECOND LAW

It has been observed that *energy can flow* from a system in the form of *heat or work*. The first law of thermodynamics sets no limit to the amount of the total energy of a system which can be caused to flow out as work. A limit is imposed, however, as a result of the principle enunciated in the second law of thermodynamics which states that heat will flow naturally from one energy reservoir to another at a lower temperature, but not in opposite direction without assistance. This is very important because a heat engine operates between two energy reservoirs at different temperatures.

Further the first law of thermodynamics establishes equivalence between the quantity of heat used and the mechanical work but does not specify the conditions under which conversion of heat into work is possible, neither the direction in which heat transfer can take place. This gap has been bridged by the second law of thermodynamics.

3.2. PERFORMANCE OF HEAT ENGINE AND REVERSED HEAT ENGINE

Refer Fig. 3.1 (a). A *heat engine* is used to produce the maximum work transfer from a given positive heat transfer. The measure of success is called the *thermal efficiency* of the engine and is defined by the ratio :

$$\text{Thermal efficiency, } \eta_{th} = \frac{W}{Q_1} \quad \dots(3.1)$$

where W = net work transfer from the engine, and

Q_1 = heat transfer to engine.

For a *reversed heat engine* [Fig. 3.1 (b)] acting as a *refrigerator* when the purpose is to achieve the maximum heat transfer from the cold reservoir, the measure of success is called the co-efficient of performance (C.O.P.). It is defined by the ratio :

$$\text{Co-efficient of performance, } (\text{C.O.P.})_{ref} = \frac{Q_2}{W} \quad \dots(3.2)$$

where Q_2 = heat transfer from cold reservoir

W = the net work transfer to the refrigerator.

SECOND LAW OF THERMODYNAMICS AND ENTROPY

For a reversed heat engine [Fig. 3.1 (b)] acting as a *heat pump*, the measure of success is again called the *co-efficient of performance*. It is defined by the ratio :

$$\text{Co-efficient of performance, } (\text{C.O.P.})_{\text{heat pump}} = \frac{Q_1}{W} \quad \dots(3.3)$$

where Q_1 = heat transfer to hot reservoir

W = net work transfer to the heat pump.

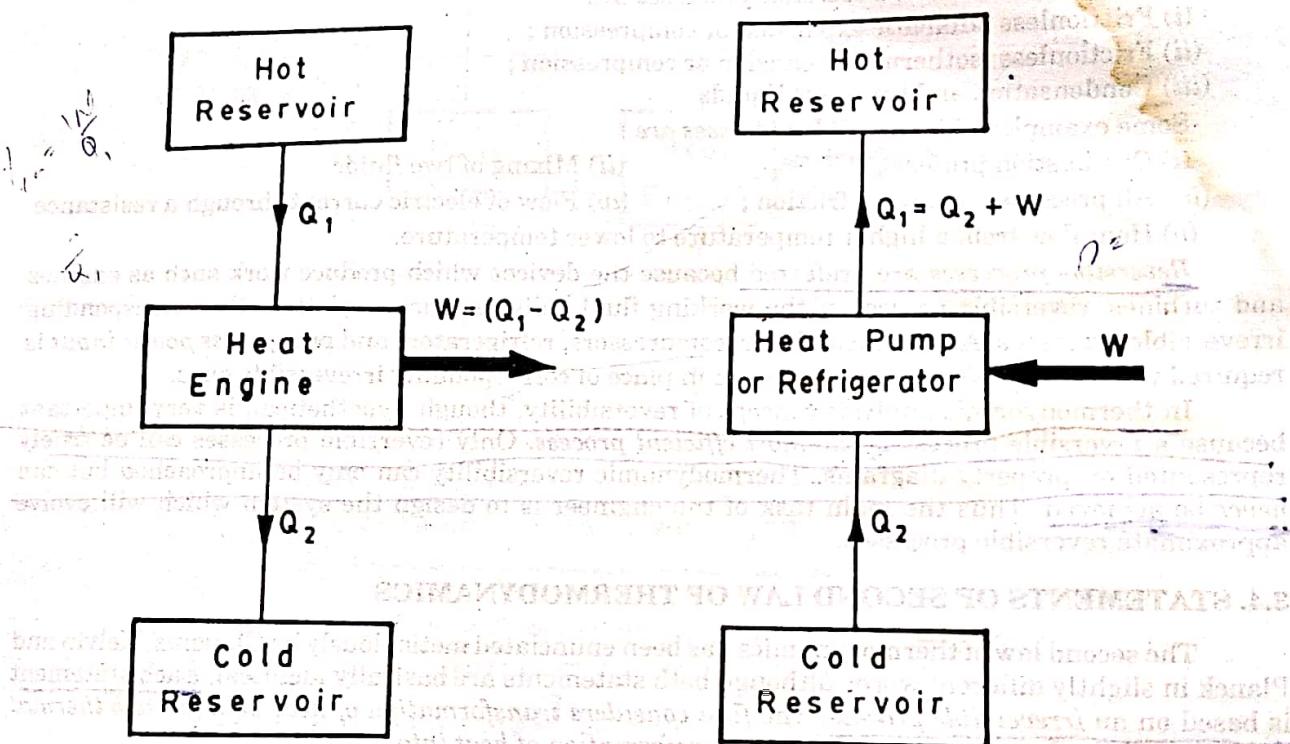


Fig. 3.1 (a) Heat engine (b) Heat pump or refrigerator

In all the above three cases application of the first law gives the relation $Q_1 - Q_2 = W$, and this can be used to rewrite the expressions for thermal efficiency and co-efficient of performance solely in terms of the heat transfers.

$$\eta_{th} = \frac{Q_1 - Q_2}{Q_1} \quad \dots(3.4)$$

$$(\text{C.O.P.})_{ref} = \frac{Q_2}{Q_1 - Q_2} \quad \dots(3.5)$$

$$(\text{C.O.P.})_{\text{heat pump}} = \frac{Q_1}{Q_1 - Q_2} \quad \dots(3.6)$$

It may be seen that η_{th} is always less than unity and $(\text{C.O.P.})_{\text{heat pump}}$ is always greater than unity.

3.3. REVERSIBLE PROCESSES

A reversible process should fulfill the following conditions :

- 1. The process should not involve friction of any kind.

2. Heat transfer should not take place with finite temperature difference.
3. The energy transfer as heat and work during the forward process should be identically equal to energy transfer as heat and work during the reversal of the process.
4. There should be no free or unrestricted expansion.
5. There should be no mixing of the fluids.
6. The process must proceed in a series of equilibrium states.

Some examples of *ideal reversible processes* are :

- (i) Frictionless adiabatic expansion or compression ;
- (ii) Frictionless isothermal expansion or compression ;
- (iii) Condensation and boiling of liquids.

Some examples of *irreversible processes* are :

- | | |
|---|--|
| (i) Combustion process ; | (ii) Mixing of two fluids |
| (iii) All processes involving friction ; | (iv) Flow of electric current through a resistance |
| (v) Heat flow from a higher temperature to lower temperature. | |

Reversible processes are preferred because the devices which produce work such as engines and turbines, reversible process of the working fluid delivers *more work* than the corresponding irreversible processes. Also in case of fans, compressors, refrigerators and pumps *less power input* is required when *reversible processes* are used in place of corresponding irreversible ones.

In thermodynamic analysis concept of reversibility, though hypothetical, is very important because a reversible process is the *most efficient process*. Only reversible processes can be truly represented on property diagrams. Thermodynamic reversibility can only be approached but can never be achieved. Thus the main task of the engineer is to design the system which will evolve approximate reversible processes.

3.4. STATEMENTS OF SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics has been enunciated meticulously by Clausius, Kelvin and Planck in slightly different words although both statements are basically identical. Each statement is based on an *irreversible process*. The first considers transformation of heat between two thermal reservoirs while the second considers the transformation of heat into work.

3.4.1. Clausius Statement

"It is impossible for a self acting machine working in a cyclic process unaided by any external agency, to convey heat from a body at a lower temperature to a body at a higher temperature".

In other words, heat of, itself, cannot flow from a colder to a hotter body.

3.4.2. Kelvin-Planck Statement

"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".

Although the Clausius and Kelvin-Planck statements appear to be different, they are really equivalent in the sense that a violation of either statement implies violation of other.

3.4.3. Equivalence of Clausius Statement to the Kelvin-Planck Statement

Refer Fig. 3.2. Consider a higher temperature reservoir T_1 and low temperature reservoir T_2 . Fig. 3.2 shows a heat pump which requires no work and transfers an amount of Q_2 from a low temperature to a higher temperature reservoir (in violation of the Clausius statement). Let an amount of heat Q_1 (greater than Q_2) be transferred from high temperature reservoir to heat engine which develops a net work, $W = Q_1 - Q_2$ and rejects Q_2 to the low temperature reservoir. Since there is no heat interaction with the low temperature, it can be eliminated. The combined system of the heat engine and heat pump acts then like a heat engine exchanging heat with a single reservoir, which is the violation of the Kelvin-Planck statement.

T₀ thermal $\rightarrow \eta \rightarrow T \text{ const.}$

SECOND LAW OF THERMODYNAMICS AND ENTROPY

is to
ach

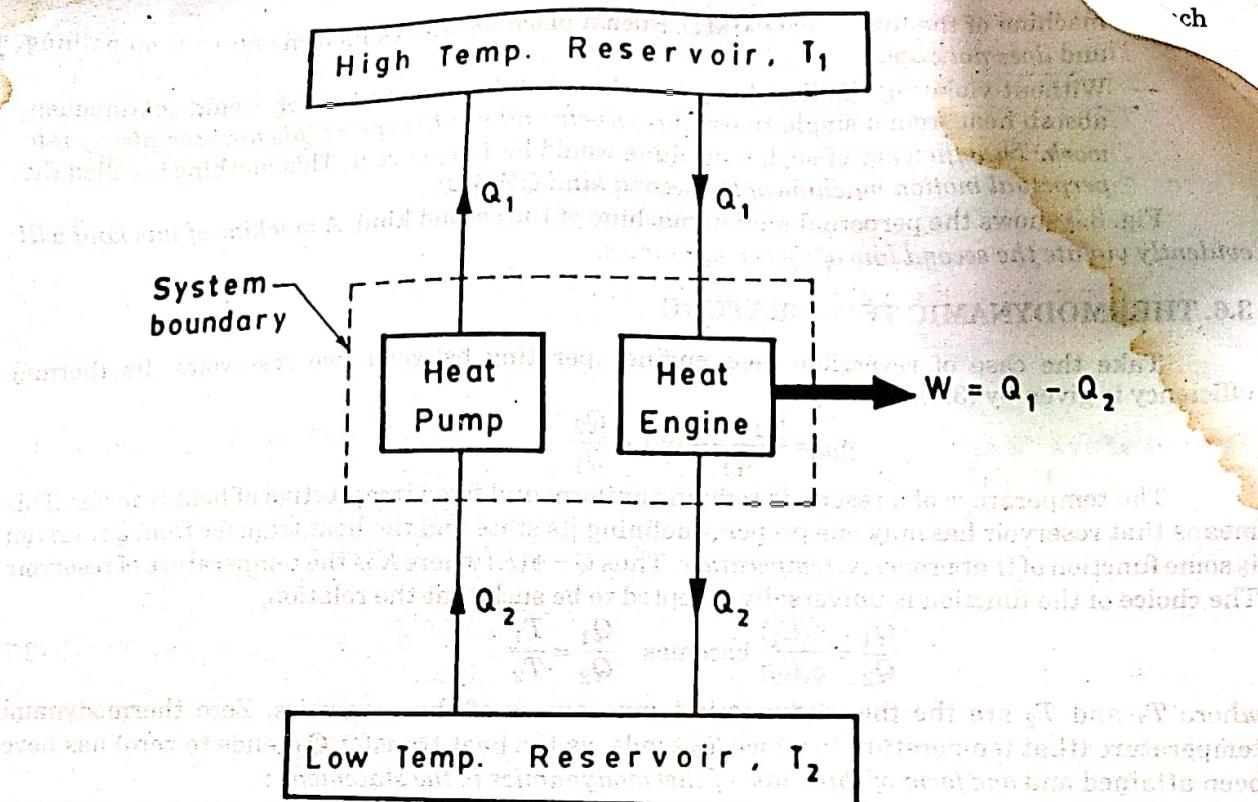


Fig. 3.2. Equivalence of Clausius statement to Kelvin-Planck statement.

3.5. PERPETUAL MOTION MACHINE OF THE SECOND KIND (PMM2)

— A machine which violates the first law of thermodynamics is called the perpetual motion machine of the second kind.

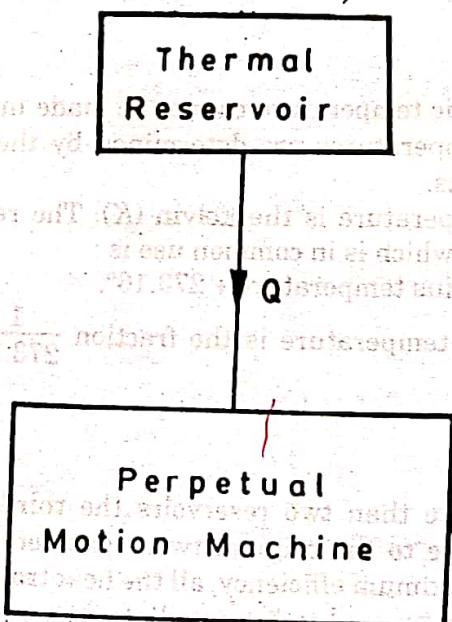


Fig. 3.3. Perpetual motion machine of second kind (PMM2).

- 2 machine of the first kind (PMM1). Such a machine creates its own energy from nothing and does not exist.
- Without violating the first law, a machine can be imagined which would continuously absorb heat from a single thermal reservoir and would convert this heat completely into work. The efficiency of such a machine would be 100 per cent. This machine is called the perpetual motion machine of the second kind (PMM2).

Fig. 3.3 shows the perpetual motion machine of the second kind. A machine of this kind will evidently violate the second law of thermodynamics.

3.6. THERMODYNAMIC TEMPERATURE

Take the case of reversible heat engine operating between two reservoirs. Its thermal efficiency is given by (3.4),

$$\eta_{th} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

The temperature of a reservoir remains uniform and fixed irrespective of heat transfer. This means that reservoir has only one property defining its state and the heat transfer from a reservoir is some function of that property, *temperature*. Thus $Q = \phi(K)$ where K is the temperature of reservoir. The choice of the function is universally accepted to be such that the relation,

$$\frac{Q_1}{Q_2} = \frac{\phi(K_1)}{\phi(K_2)} \text{ becomes } \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \dots(3.7)$$

where T_1 and T_2 are the thermodynamic temperatures of the reservoirs. Zero thermodynamic temperature (that temperature to which T_2 tends, as the heat transfer Q_2 tends to zero) has never been attained and one form of third law of thermodynamics is the statement :

"The temperature of a system cannot be reduced to zero in a finite number of processes."

After establishing the concept of a zero thermodynamic temperature, a reference reservoir is chosen and assigned a numerical value of temperature. Any other thermodynamic temperature may now be defined in terms of reference value and the heat transfers that would occur with reversible engine,

$$T = T_{ref} \cdot \frac{Q}{Q_{ref}} \quad \dots(3.8)$$

The determination of thermodynamic temperature cannot be made in this way as it is not possible to build a reversible engine. Temperatures are determined by the application of thermodynamic relations to other measurements.

The SI unit of thermodynamic temperature is the kelvin (K). The relation between thermodynamic temperature and celsius scale, which is in common use is :

$$\text{Thermodynamic temperature} = \text{Celsius temperature} + 273.16^\circ$$

The kelvin unit of thermodynamic temperature is the fraction $\frac{1}{273.16}$ of thermodynamic temperature of 'Triple point' of water.

3.7. CLAUSIUS INEQUALITY

When a reversible engine uses more than two reservoirs the third or higher numbered reservoirs will not be equal in temperature to the original two. Consideration of expression for efficiency of the engine indicates that for maximum efficiency, all the heat transfer should take place at maximum or minimum reservoir temperatures. Any intermediate reservoir used will, therefore, lower the efficiency of the heat engine. Practical engine cycles often involve continuous changes of temperature during heat transfer. A relationship among processes in which these sort of changes

SECOND LAW OF THERMODYNAMICS AND ENTROPY

occur is necessary. The ideal approach to a cycle in which temperature continually changes is to consider the system to be in communication with a large number of reservoirs in procession. Each reservoir is considered to have a temperature differing by a small amount from the previous one. In such a model it is possible to imagine that each reservoir is replaced by a reversible heat engine in communication with standard reservoirs at same temperature T_0 . Fig. 3.4 shows one example to this substitution.

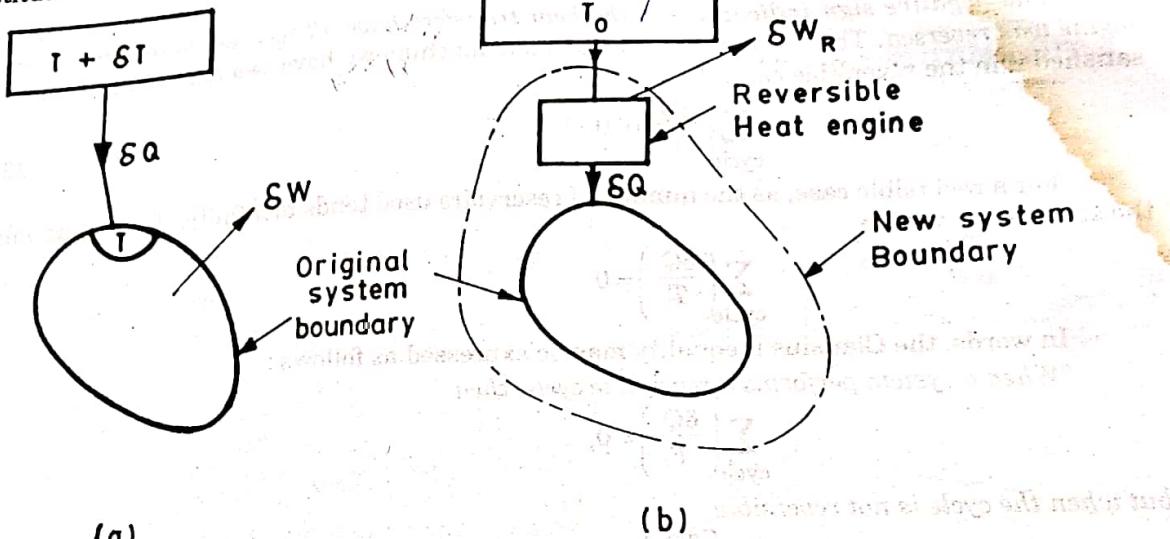


Fig. 3.4. The clausius inequality.

The system to which the heat transfer is effected is neither concerned with the source of energy it receives nor with the method of transfer, save that it must be reversible. Associated with the small heat transfer dQ to the original system is a small work transfer dW and for this system the first law gives

$$\sum_{\text{cycle}} (\delta Q - \delta W) = 0 \quad \dots(3.9)$$

Now consider the engine replacing the reservoirs and apply the second law to the new system in Fig. 3.4 (b). If the new system is not a perpetual motion machine of second kind, no positive work transfer is possible with a single reservoir.

Therefore,

$$\sum_{\text{cycle}} (\delta W - \delta W_R) \leq 0 \quad \dots(3.10)$$

But by the definition of thermodynamic temperature in equation (3.8)

$$\frac{\delta W_R}{\delta Q} = \frac{\delta Q_f - \delta Q_i}{\delta Q} = \frac{T_0 - T}{T} \quad \dots(3.11)$$

and by combination of equations (3.9), (3.10) and (3.11)

$$T_0 \sum_{\text{cycle}} \left(\frac{\delta Q}{T} \right) \leq 0 \text{ but } T_0 \neq 0 \text{ and therefore ;}$$

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T} \right) \leq 0 \quad \checkmark \quad \dots(3.12)$$

This is known as **Clausius inequality**.

Let us now consider the case of a reversible engine for which

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T} \right) \leq 0,$$

reverse the engine and for the reversible heat pump obtained it is possible to develop the expression,

$$-\sum_{\text{cycle}} \left(\frac{\delta Q}{T} \right) \leq 0$$

The negative sign indicates that the heat transfers have all reversed in direction when the engine was reversed. This means that for the same machine we have two relations which are only satisfied if in the reversible case,

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T} \right) \leq 0 \quad \dots(3.13)$$

For a reversible case, as the number of reservoirs used tends to infinity, the limiting value of the summation will be

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T} \right) = 0$$

In words, the Clausius inequality may be expressed as follows :
"When a system performs a reversible cycle, then

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T} \right) = 0,$$

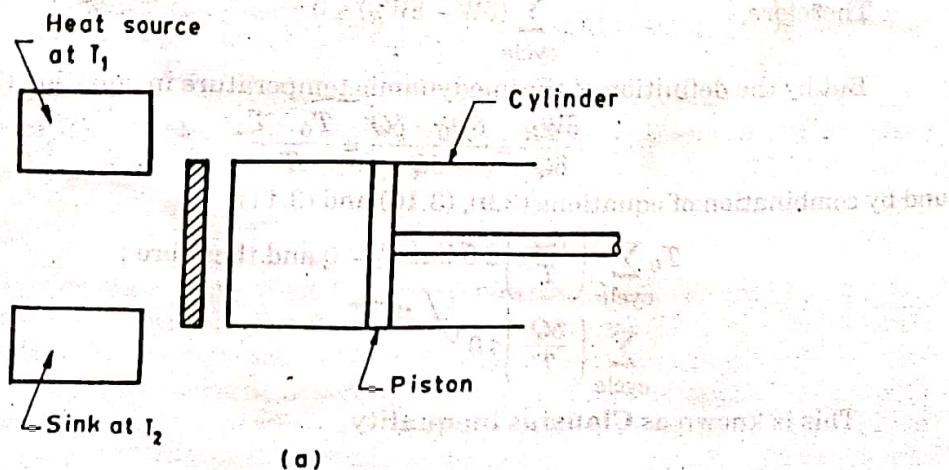
but when the cycle is not reversible

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T} \right) < 0.$$

3.8. CARNOT CYCLE

The cycle was first suggested by a French engineer Sadi Carnot in 1824 which works on reversible cycle and is known as *Carnot cycle*.

Any fluid may be used to operate the Carnot cycle (Fig. 3.5) which is performed in an engine cylinder the head of which is supposed alternatively to be perfect conductor or a perfect insulator of a heat. Heat is caused to flow into the cylinder by the application of high temperature energy source to the cylinder head during expansion, and to flow from the cylinder by the application of a lower temperature energy source to the head during compression.



Such an engine since it consists entirely of reversible processes, can operate in the reverse direction so that it follows the cycle shown in Fig. 3.5 (b) and operates as a **heat pump**. Q_2 is being taken in at the lower temperature T_2 during the isothermal expansion (process 4-3) and heat Q_1 is being rejected at the upper temperature T_1 (process 2-1). Work W will be needed to drive the pump. Again, the enclosed area represents this work which is exactly equal to that flowing from it when used as engine.

The Carnot cycle *cannot be performed in practice* because of the following **reasons**:

1. It is impossible to perform a frictionless process.

2. It is impossible to transfer the heat without temperature potential.

3. Isothermal process can be achieved only if the piston moves very slowly to allow heat transfer so that the temperature remains constant. Adiabatic process can be achieved only if the piston moves as fast as possible so that the heat transfer is negligible due to very short time available. The isothermal and adiabatic processes take place during the same stroke therefore the piston has to move very slowly for part of the stroke and it has to move very fast during remaining stroke. This variation of motion of the piston during the same stroke is not possible.

3.9. CARNOT'S THEOREM

"It states that of all engines operating between a given constant temperature source and a given constant temperature sink, none has a higher efficiency than a reversible engine".

Refer Fig. 3.6.

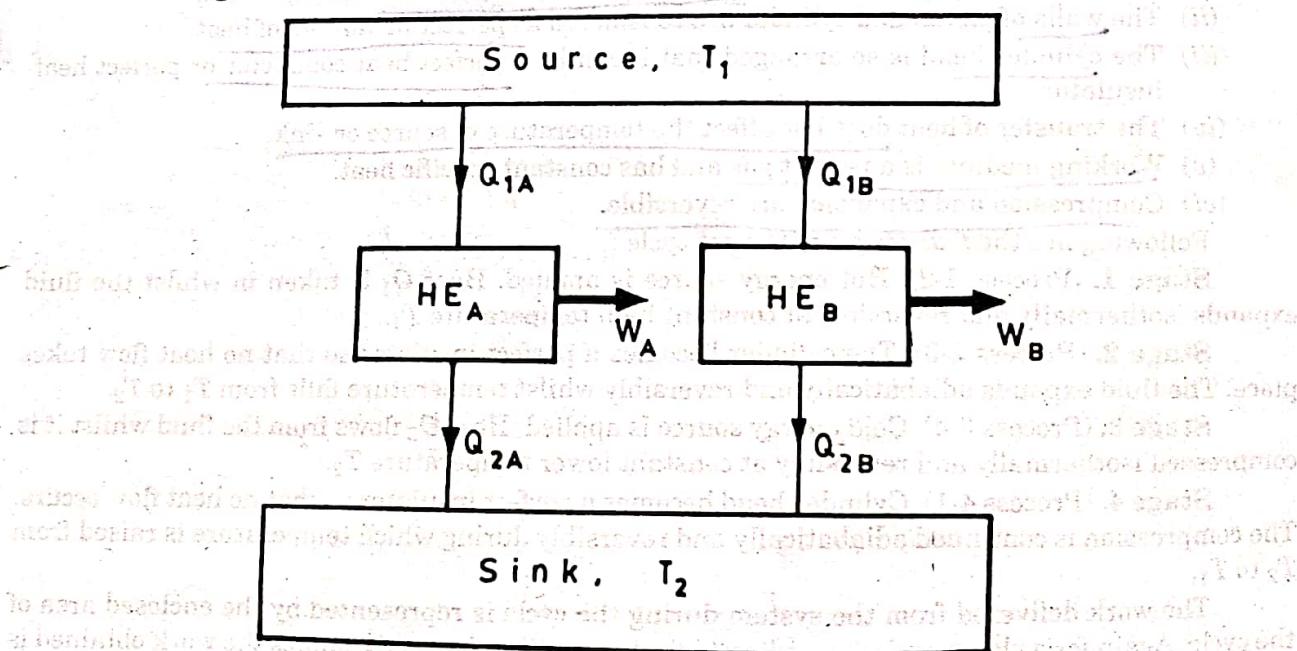


Fig. 3.6. Two cyclic heat engines HE_A and HE_B operating between the same source and sink, of which HE_B is reversible.

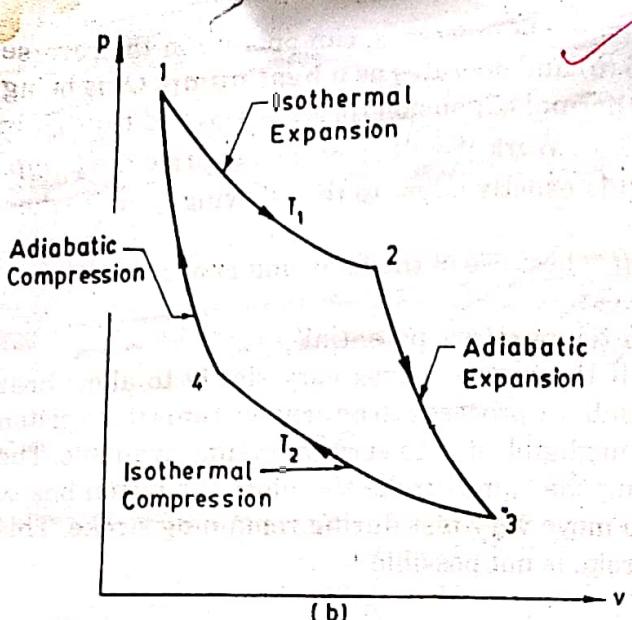
HE_A and HE_B are the two engines operating between the given source at temperature T_1 and the given sink at temperature T_2 .

Let HE_A be *any* heat engine and HE_B be *any reversible* heat engine. We have to prove that efficiency of HE_B is more than that of HE_A . Let us assume that $\eta_A > \eta_B$. Let the rates of working of the engines be such that

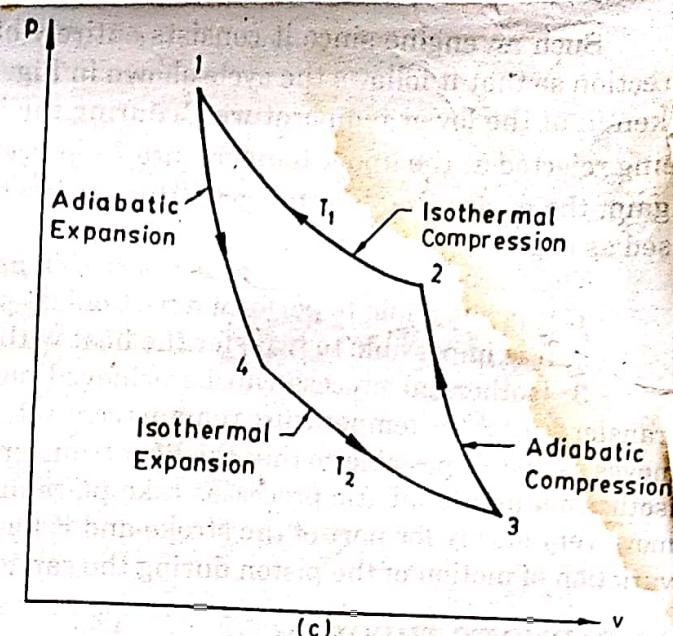
$$Q_{1A} = Q_{1B} = Q_1$$

SECOND LAW OF THERMODYNAMICS AND ENTROPY

REFRIGERATION



Carnot engine cycle



Carnot heat pump cycle

Fig. 3.5

The assumptions made for describing the working of the Carnot engine are as follows :

- The piston moving in a cylinder does not develop any friction during motion.
- The walls of piston and cylinder are considered as perfect insulators of heat.
- The cylinder head is so arranged that it can be a perfect heat conductor or perfect heat insulator.
- The transfer of heat does not affect the temperature of source or sink.
- Working medium is a perfect gas and has constant specific heat.
- Compression and expansion are reversible.

Following are the four stages of Carnot cycle :

Stage 1. (Process 1-2). Hot energy source is applied. Heat Q_1 is taken in whilst the fluid expands isothermally and reversibly at constant high temperature T_1 .

Stage 2. (Process 2-3). The cylinder becomes a perfect insulator so that no heat flow takes place. The fluid expands adiabatically and reversibly whilst temperature falls from T_1 to T_2 .

Stage 3. (Process 3-4). Cold energy source is applied. Heat Q_2 flows from the fluid whilst it is compressed isothermally and reversibly at constant lower temperature T_2 .

Stage 4. (Process 4-1). Cylinder head becomes a perfect insulator so that no heat flow occurs. The compression is continued adiabatically and reversibly during which temperature is raised from T_2 to T_1 .

The work delivered from the system during the cycle is represented by the enclosed area of the cycle. Again for a closed cycle, according to first law of the thermodynamics the work obtained is equal to the difference between the heat supplied by the source (Q_1) and the heat rejected to the sink (Q_2).

$$W = Q_1 - Q_2$$

Also, thermal efficiency, $\eta_{th} = \frac{\text{work done}}{\text{heat supplied by the source}} = \frac{Q_1 - Q_2}{Q_1}$

$$= 1 - \frac{Q_2}{Q_1} \left(= 1 - \frac{T_2}{T_1} \right)$$

$$\begin{aligned} Q_1 &= m c_p T_1 \\ Q_2 &= m c_p T_2 \\ \text{where } m &= \text{mass of fluid} \end{aligned}$$

line which, operating in a cycle produces net work $W_A - W_B$ while exchanging heat with a single reservoir at T_2 . This violates the Kelvin-Planck statement of the second law. Hence the assumption that $\eta_A > \eta_B$ is wrong.

$$\eta_B \geq \eta_A$$

3.10. COROLLARY OF CARNOT'S THEOREM

"The efficiency of all reversible heat engines operating between the same temperature levels is the same".

Refer Fig. 3.6. Let both the heat engines HE_A and HE_B be reversible. Let us assume $\eta_A > \eta_B$. Similar to the procedure outlined in the Article 3.9, if HE_B is reversed to run say, as a heat pump using some part of the work output (W_A) of engine HE_A , we see that the combined system of heat pump HE_B and engine HE_A , becomes a PMM2. So η_A cannot be greater than η_B . Similarly, if we assume $\eta_B > \eta_A$ and reverse the engine HE_A , we observe that η_B cannot be greater than η_A .

$$\eta_A = \eta_B$$

Since the efficiencies of all reversible engines operating between the same heat reservoirs are the same, the efficiency of a reversible engine is independent of the nature or amount of the working substance undergoing the cycle.

3.11. EFFICIENCY OF THE REVERSIBLE HEAT ENGINE

The efficiency of a reversible heat engine in which heat is received solely at T_1 is found to be

$$\eta_{rev.} = \eta_{max} = 1 - \left(\frac{Q_2}{Q_1} \right)_{rev.} = 1 - \frac{T_2}{T_1}$$

or

$$\eta_{rev.} = \frac{T_1 - T_2}{T_1}$$

From the above expression, it may be noted that as T_2 decreases and T_1 increases, the efficiency of the reversible cycle increases.

Since η is always less than unity, T_2 is always greater than zero and + ve.

The C.O.P. of a refrigerator is given by

$$(C.O.P.)_{ref.} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

For a reversible refrigerator, using

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

$$(C.O.P.)_{rev.} = \frac{1}{\frac{T_1}{T_2} - 1}$$

$$\therefore [(C.O.P.)_{ref.}]_{rev.} = \frac{T_2}{T_1 - T_2} \quad \checkmark$$

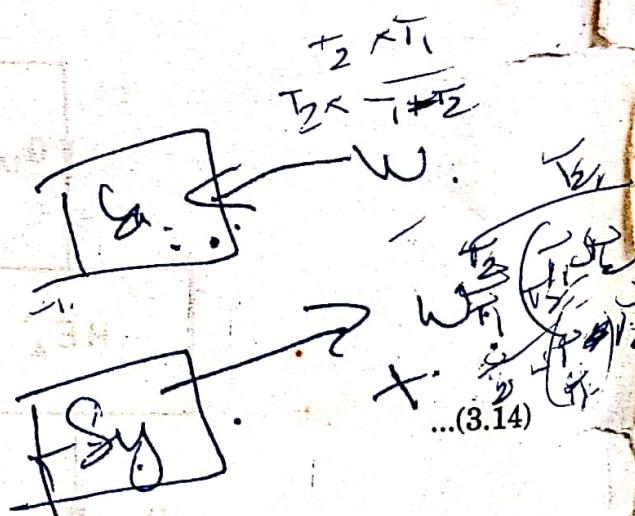
Similarly, for a reversible heat pump

$$[(C.O.P.)_{heat\ pump}]_{rev.} = \frac{T_1}{T_1 - T_2} \quad \checkmark$$

Example 3.1. A heat engine receives heat at the rate of 1500 kJ/min and gives an output of

8.2 kW. Determine:

- (i) The thermal efficiency;
- (ii) The rate of heat rejection.



... (3.14)

... (3.15)

SECOND LAW OF THERMODYNAMICS AND ENTROPY

Since

$$\eta_A > \eta_B$$

$$W_A > W_B$$

$$\frac{W_A}{Q_{1A}} > \frac{W_B}{Q_{1B}}$$

$$W_A > W_B$$

Now, let HE_B be reversed. Since HE_B is a reversible heat engine, the magnitudes of heat and work transfer quantities will remain the same, but their directions will be reversed, as shown in Fig. 3.7. Since $W_A > W_B$, some part of W_A (equal to W_B) may be fed to drive the reversed heat engine $\exists H_B$. Since $Q_{1A} = Q_{1B} = Q_1$, the heat discharged by $\exists H_B$ may be supplied to HE_A . The source may, therefore, be eliminated (Fig. 3.8). The net result is that HE_A and $\exists H_B$ together constitute a heat pump.

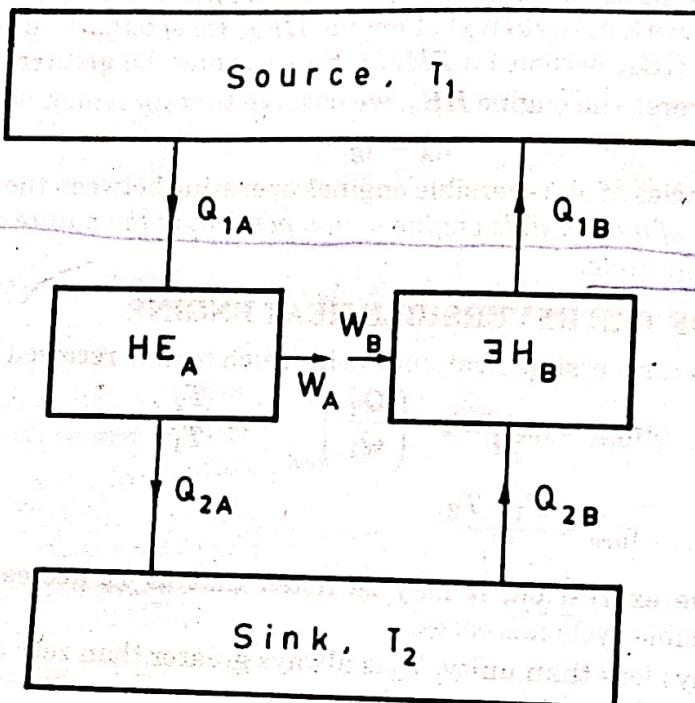


Fig. 3.7. HE_B is reversed.

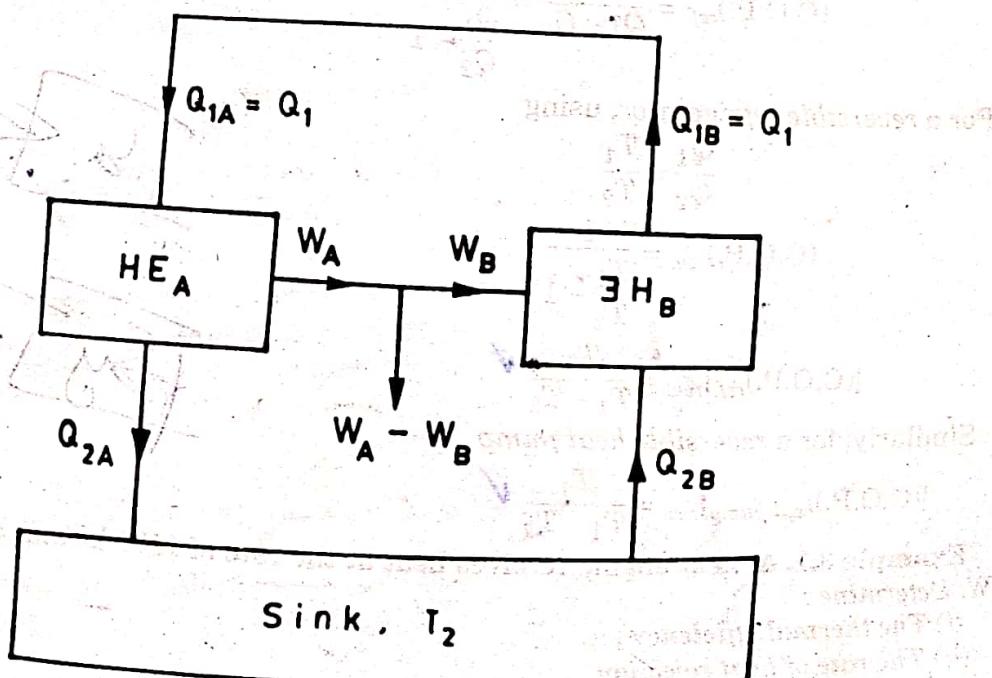


Fig. 3.8. HE_A and $\exists H_B$ together violate the Kelvin-Planck statement.

SECOND LAW OF THERMODYNAMICS AND ENTROPY

179

Solution. Heat received by the heat engine,

$$Q_1 = 1500 \text{ kJ/min}$$

$$= \frac{1500 \times 1000}{60} = 25 \times 10^3 \text{ J/s}$$

$$\text{Work output, } W = 8.2 \text{ kW} = 8.2 \times 10^3 \text{ W or J/s.}$$

$$(i) \text{ Thermal efficiency, } \eta_{th} = \frac{W}{Q_1}$$

$$= \frac{8.2 \times 10^3}{25 \times 10^3} = 0.328 = 32.8\%$$

Hence, thermal efficiency = 32.8%. (Ans.)

(ii) Rate of heat rejection,

$$Q_2 = Q_1 - W = 25 \times 10^3 - 8.2 \times 10^3$$

$$= 16.8 \times 10^3 \text{ J/s} = 16.8 \text{ kJ/s}$$

Hence, the rate of heat rejection = 16.8 kJ/s. (Ans.)

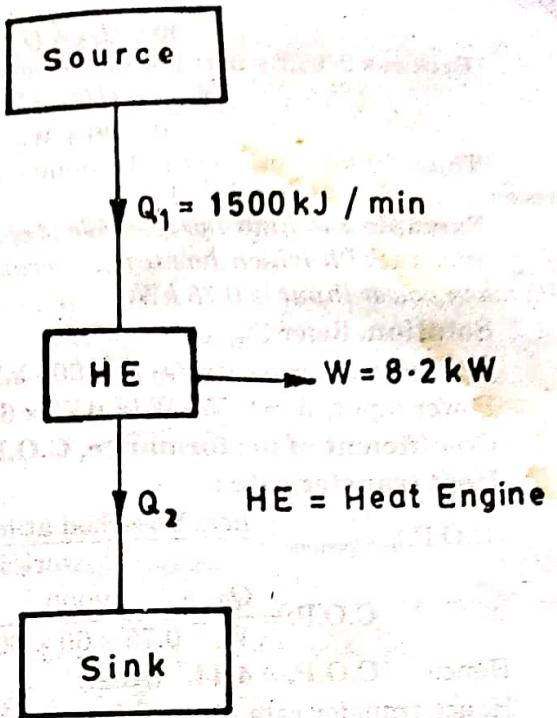


Fig. 3.9

Example 3.2. During a process a system receives 30 kJ of heat from a reservoir and does 60 kJ of work. Is it possible to reach initial state by an adiabatic process?

Solution. Heat received by the system = 30 kJ

Work done = 60 kJ

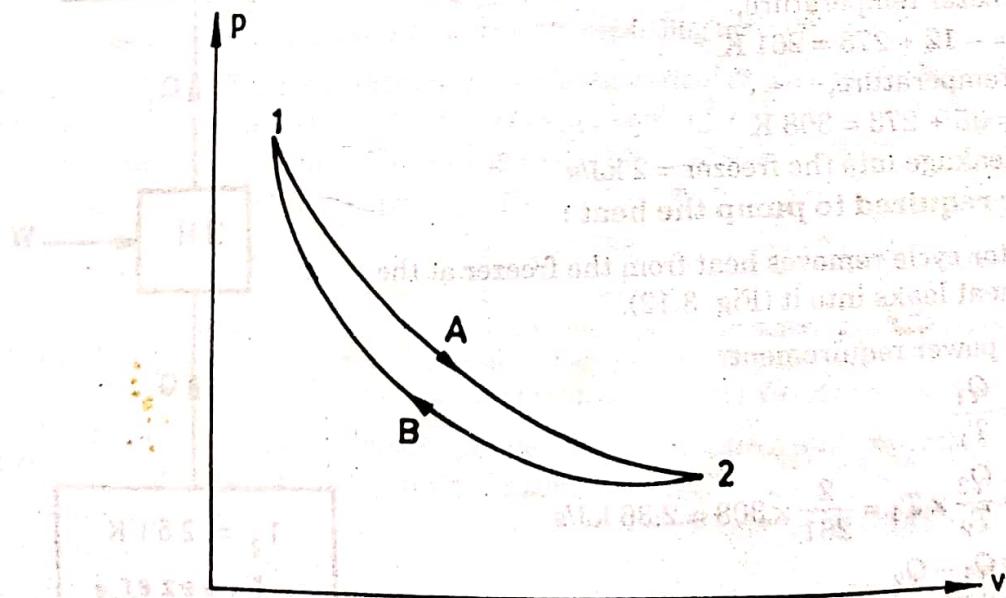


Fig. 3.10

Process 1-2 : By first law of thermodynamics

$$Q_{1-2} = (U_2 - U_1) + W_{1-2}$$

$$30 = (U_2 - U_1) + 60 \therefore (U_2 - U_1) = -30 \text{ kJ.}$$

Process 2-1 : By first law of thermodynamics

$$Q_{2-1} = (U_1 - U_2) + W_{2-1}$$

$$\therefore 0 = 30 + W_{2-1} \therefore W_{2-1} = -30 \text{ kJ.}$$

Thus 30 kJ work has to be done on the system to restore it to original state, by adiabatic process.

Example 3.3. Find the co-efficient of performance and heat transfer rate in the condenser of a refrigerator in kJ/h which has a refrigeration capacity of 12000 kJ/h when power input is 0.75 kW.

Solution. Refer Fig. 3.11.

Refrigeration capacity, $Q_2 = 12000 \text{ kJ/h}$

Power input, $W = 0.75 \text{ kW} (= 0.75 \times 60 \times 60 \text{ kJ/h})$

Co-efficient of performance, C.O.P. :

Heat transfer rate :

$$(\text{C.O.P.})_{\text{refrigerator}} = \frac{\text{heat absorbed at lower temperature}}{\text{work input}}$$

$$\therefore \text{C.O.P.} = \frac{Q_2}{W} = \frac{12000}{0.75 \times 60 \times 60} = 4.44$$

Hence **C.O.P. = 4.44. (Ans.)**

Hence transfer rate in condenser = Q_1

According to the first law

$$Q_1 = Q_2 + W = 12000 + 0.75 \times 60 \times 60 = 14700 \text{ kJ/h}$$

Hence, heat transfer rate = 14700 kJ/h . (Ans.)

Example 3.4. A domestic food refrigerator maintains a temperature of -12°C . The ambient air temperature is 35°C . If heat leaks into the freezer at the continuous rate of 2 kJ/s determine the least power necessary to pump this heat out continuously.

Solution. Freezer temperature,

$$T_2 = -12 + 273 = 261 \text{ K}$$

Ambient air temperature,

$$T_1 = 35 + 273 = 308 \text{ K}$$

Rate of heat leakage into the freezer = 2 kJ/s

Least power required to pump the heat :

The refrigerator cycle removes heat from the freezer at the same rate at which heat leaks into it (Fig. 3.12).

For minimum power requirement

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

$$\therefore Q_1 = \frac{Q_2}{T_2} \times T_1 = \frac{2}{261} \times 308 = 2.36 \text{ kJ/s}$$

$$\therefore W = Q_1 - Q_2 \\ = 2.36 - 2 = 0.36 \text{ kJ/s} = 0.36 \text{ kW}$$

Hence, least power required to pump the heat continuously

$$= 0.36 \text{ kW. (Ans.)}$$

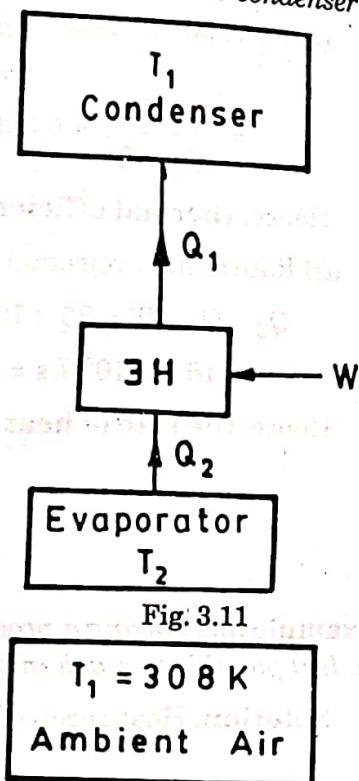


Fig. 3.11

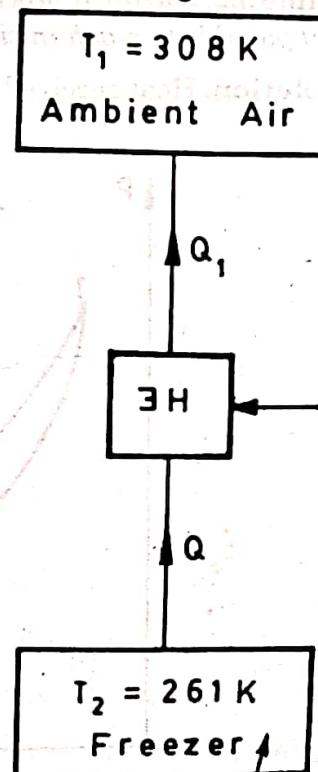


Fig. 3.12

SECOND LAW OF THERMODYNAMICS AND ENTROPY

Example 3.5. A house requires $2 \times 10^5 \text{ kJ/h}$ for heating in winter. Heat pump is used to absorb heat from cold air outside in winter and send heat to the house. Work required to operate the heat pump is $3 \times 10^4 \text{ kJ/h}$. Determine :

(i) Heat abstracted from outside ;

(ii) Co-efficient of performance.

Solution. (i) Heat requirement of the house, Q_1 (or heat rejected)

$$= 2 \times 10^5 \text{ kJ/h}$$

Work required to operate the heat pump,

$$W = 3 \times 10^4 \text{ kJ/h}$$

Now,

$$Q_1 = W + Q_2$$

where Q_2 is the heat abstracted from outside.

$$\therefore 2 \times 10^5 = 3 \times 10^4 + Q_2$$

Thus

$$Q_2 = 2 \times 10^5 - 3 \times 10^4$$

$$= 200000 - 30000 = 170000 \text{ kJ/h}$$

Hence, heat abstracted from outside = 170000 kJ/h . (Ans.)

$$(ii) (\text{C.O.P.})_{\text{heat pump}} = \frac{Q_1}{Q_1 - Q_2}$$

$$= \frac{2 \times 10^5}{2 \times 10^5 - 170000} = 6.66$$

Hence, co-efficient of performance = 6.66. (Ans.)

Note. If the heat requirements of the house were the same but this amount of heat had to be abstracted from the house and rejected out, i.e. cooling of the house in summer, we have

$$(\text{C.O.P.})_{\text{refrigerator}} = \frac{Q_2}{Q_1 - Q_2} = \frac{Q_2}{W}$$

$$= \frac{170000}{3 \times 10^4} = 5.66$$

Thus the same device has two values of C.O.P. depending upon the objective.

Example 3.6. What is the highest possible theoretical efficiency of a heat engine operating with a hot reservoir of furnace gases at 2100°C when the cooling water available is at 15°C ?

Solution. Temperature of furnace gases, $T_1 = 2100 + 273 = 2373 \text{ K}$

Temperature of cooling water, $T_2 = 15 + 273 = 288 \text{ K}$

$$\text{Now, } \eta_{\text{max}} (= \eta_{\text{carnot}}) = 1 - \frac{T_2}{T_1} = 1 - \frac{288}{2373} = 0.878 \text{ or } 87.8\%. \text{ (Ans.)}$$

Note. It should be noted that a system in practice operating between similar temperatures (e.g. a steam generating plant) would have a thermal efficiency of about 30%. The discrepancy is due to irreversibility in the actual plant, and also because of deviations from the ideal Carnot cycle made for various practical reasons.

Example 3.7. A Carnot cycle operates between source and sink temperatures of 250°C and -15°C . If the system receives 90 kJ from the source, find :

(i) Efficiency of the system ;

(ii) The net work transfer ;

(iii) Heat rejected to sink.

Solution. Temperature of source, $T_1 = 250 + 273 = 523 \text{ K}$

Temperature of sink, $T_2 = -15 + 273 = 258 \text{ K}$

Heat received by the system, $Q_1 = 90 \text{ kJ}$

$$(i) \eta_{\text{carnot}} = 1 - \frac{T_2}{T_1} = 1 - \frac{258}{523} = 0.506 = 50.6\%. \text{ (Ans.)}$$

(ii) The net work transfer, $W = \eta_{\text{carnot}} \times Q_1$
 $= 0.506 \times 90 = 45.54 \text{ kJ. (Ans.)}$

(iii) Heat rejected to the sink, $Q_2 = Q_1 - W$
 $= 90 - 45.54 = 44.46 \text{ kJ. (Ans.)}$

Example 3.8. An inventor claims that his engine has the following specifications :

Temperature limits 750°C and 25°C

Power developed 75 kW

Fuel burned per hour 3.9 kg

Heating value of the fuel 74500 kJ/kg

State whether his claim is valid or not.

Solution. Temperature of source, $T_1 = 750 + 273 = 1023 \text{ K}$

Temperature of sink, $T_2 = 25 + 273 = 298 \text{ K}$

We know that the thermal efficiency of Carnot cycle is the maximum between the specified temperature limits.

Now, $\eta_{\text{carnot}} = 1 - \frac{T_2}{T_1} = 1 - \frac{298}{1023} = 0.7086 \text{ or } 70.86\%$

The actual thermal efficiency claimed,

$$\eta_{\text{thermal}} = \frac{\text{work done}}{\text{heat supplied}} = \frac{75 \times 1000 \times 60 \times 60}{3.9 \times 74500 \times 1000} = 0.9292 \text{ or } 92.92\%.$$

Since $\eta_{\text{thermal}} > \eta_{\text{carnot}}$, therefore claim of the inventor is not valid (or possible). (Ans.)

Example 3.9. A cyclic heat engine operates between a source temperature of 1000°C and a sink temperature of 40°C . Find the least rate of heat rejection per kW net output of the engine ?

Solution. Temperature of source,

$$T_1 = 1000 + 273 = 1273 \text{ K}$$

Temperature of sink,

$$T_2 = 40 + 273 = 313 \text{ K}$$

Least rate of heat rejection per kW net output:

For a reversible heat engine, the rate of heat rejection will be minimum (Fig. 3.13)

$$\eta_{\text{max}} = \eta_{\text{rev.}} = 1 - \frac{T_2}{T_1}$$

$$= 1 - \frac{313}{1273} = 0.754$$

$$\text{Now } \frac{W_{\text{net}}}{Q_1} = \eta_{\text{max}} = 0.754$$

$$\therefore Q_1 = \frac{W_{\text{net}}}{0.754} = \frac{1}{0.754} = 1.326 \text{ kW}$$

$$\text{Now } Q_2 = Q_1 - W_{\text{net}} = 1.326 - 1 \\ = 0.326 \text{ kW}$$

$$\text{Hence, the least rate of heat rejection} \\ = 0.326 \text{ kW. (Ans.)}$$

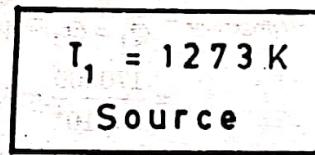


Fig. 3.13

Example 3.10. A fish freezing plant requires 40 tons of refrigeration. The freezing temperature is -35°C while the ambient temperature is 30°C . If the performance of the plant is 20% of the theoretical reversed Carnot cycle working within the same temperature limits, calculate the power required.

Given : 1 ton of refrigeration = 210 kJ/min

Solution. Cooling required = $40 \text{ tons} = 40 \times 210 = 8400 \text{ kJ/min}$

Ambient temperature, $T_1 = 30 + 273 = 303 \text{ K}$

Freezing temperature, $T_2 = -35 + 273 = 238 \text{ K}$

Performance of plant = 20% of the theoretical reversed Carnot cycle

$$(\text{C.O.P.})_{\text{refrigerator}} = \frac{T_2}{T_1 - T_2} = \frac{238}{303 - 238} = 3.66$$

$$\therefore \text{Actual C.O.P.} = 0.20 \times 3.66 = 0.732$$

Now work needed to produce cooling of 40 tons is calculated as follows :

$$(\text{C.O.P.})_{\text{actual}} = \frac{\text{cooling reqd.}}{\text{work needed}}$$

$$0.732 = \frac{8400}{W} \quad \text{or} \quad W = \frac{8400}{0.732} \text{ kJ/min} = 11425 \text{ kJ/s} = 191.25 \text{ kW}$$

Hence, power required = 191.25 kW . (Ans.)

Example 3.11. Source 1 can supply energy at the rate of 12000 kJ/min at 320°C . A second source 2 can supply energy at the rate of 120000 kJ/min at 70°C . Which source (1 or 2) would you choose to supply energy to an ideal reversible heat engine that is to produce large amount of power if the temperature of the surroundings is 35°C ?

Solution. Source 1 :

Rate of supply of energy = 12000 kJ/min

Temperature, $T_1 = 320 + 273 = 593 \text{ K}$

Source 2 :

Rate of supply of energy = 120000 kJ/min

Temperature, $T_1 = 70 + 273 = 343 \text{ K}$

Temperature of the surroundings, $T_2 = 35^{\circ}\text{C} + 273 = 308 \text{ K}$

Let the Carnot engine be working in the two cases with the two source temperatures and the single sink temperature. The efficiency of the cycle will be given by :

$$\eta_1 = 1 - \frac{T_2}{T_1} = 1 - \frac{308}{593} = 0.4806 \text{ or } 48.06\%$$

$$\eta_2 = 1 - \frac{T_2}{T_1} = 1 - \frac{308}{343} = 0.102 \text{ or } 10.2\%$$

\therefore The work delivered in the two cases is given by

$$W_1 = 12000 \times 0.4806 = 5767.2 \text{ kJ/min}$$

$$W_2 = 120000 \times 0.102 = 12240 \text{ kJ/min.}$$

Thus, choose source 2. (Ans.)

Note. The source 2 is selected even though efficiency in this case is lower, because the criterion for selection is the larger output.

Example 3.12. A reversible heat engine operates between two reservoirs at temperatures 700°C and 50°C. The engine drives a reversible refrigerator which operates between reservoirs at temperatures of 50°C and -25°C. The heat transfer to the engine is 2500 kJ and the net work output of the combined engine refrigerator plant is 400 kJ.

- Determine the heat transfer to the refrigerant and the net heat transfer to the reservoir at 50°C;
- Reconsider (i) given that the efficiency of the heat engine and the C.O.P. of the refrigerator are each 45 per cent of their maximum possible values.

Solution. Refer Fig. 3.14.

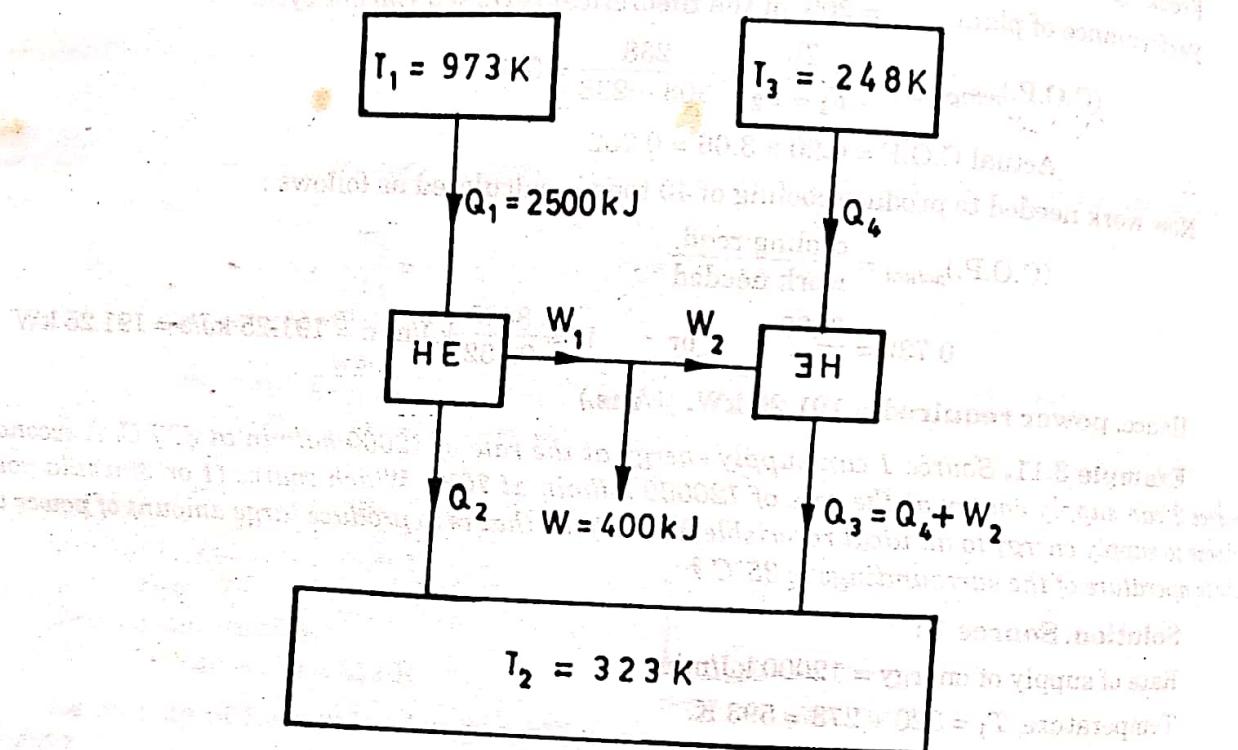


Fig. 3.14

$$\begin{aligned} \text{Temperature, } & T_1 = 700 + 273 = 973 \text{ K} \\ \text{Temperature, } & T_2 = 50 + 273 = 323 \text{ K} \\ \text{Temperature, } & T_3 = -25 + 273 = 248 \text{ K} \\ \text{The heat transfer to the heat engine, } & Q_1 = 2500 \text{ kJ} \\ \text{The network output of the combined engine refrigerator plant, off } & W = W_1 - W_2 = 400 \text{ kJ.} \end{aligned}$$

(i) Maximum efficiency of the heat engine cycle is given by

$$\eta_{max} = 1 - \frac{T_2}{T_1} = 1 - \frac{323}{973} = 0.668$$

Again,

$$\frac{W_1}{Q_1} = 0.668$$

∴

$$W_1 = 0.668 \times 2500 = 1670 \text{ kJ}$$

$$(C.O.P.)_{max} = \frac{T_3}{T_2 - T_3} = \frac{248}{323 - 248} = 3.306$$

Also,

$$C.O.P. = \frac{Q_4}{W_2} = 3.306$$

Since,

$$\begin{aligned} W_1 - W_2 &= W = 400 \text{ kJ} \\ W_2 &= W_1 - W = 1670 - 400 = 1270 \text{ kJ} \\ Q_4 &= 3.306 \times 1270 = 4198.6 \text{ kJ} \\ Q_3 &= Q_4 + W_2 = 4198.6 + 1270 = 5468.6 \text{ kJ} \\ Q_2 &= Q_1 - W_1 = 2500 - 1670 = 830 \text{ kJ.} \end{aligned}$$

Heat rejection to the 50°C reservoir
 $= Q_2 + Q_3 = 830 + 5468.6 = 6298.6 \text{ kJ. (Ans.)}$

(ii) Efficiency of actual heat engine cycle,

$$\eta = 0.45 \eta_{max} = 0.45 \times 0.668 = 0.3$$

$$W_1 = \eta \times Q_1 = 0.3 \times 2500 = 750 \text{ kJ}$$

$$W_2 = 750 - 400 = 350 \text{ kJ}$$

C.O.P. of the actual refrigerator cycle,

$$\text{C.O.P.} = \frac{Q_4}{W_2} = 0.45 \times 3.306 = 1.48$$

$$Q_4 = 350 \times 1.48 = 518 \text{ kJ. (Ans.)}$$

$$Q_3 = 518 + 350 = 868 \text{ kJ}$$

$$Q_2 = 2500 - 750 = 1750 \text{ kJ}$$

Heat rejected to 50°C reservoir

$$= Q_2 + Q_3 = 1750 + 868 = 2618 \text{ kJ. (Ans.)}$$

Example 3.13. (i) A reversible heat pump is used to maintain a temperature of 0°C in a refrigerator when it rejects the heat to the surroundings at 25°C. If the heat removal rate from the refrigerator is 1440 kJ/min, determine the C.O.P. of the machine and work input required.

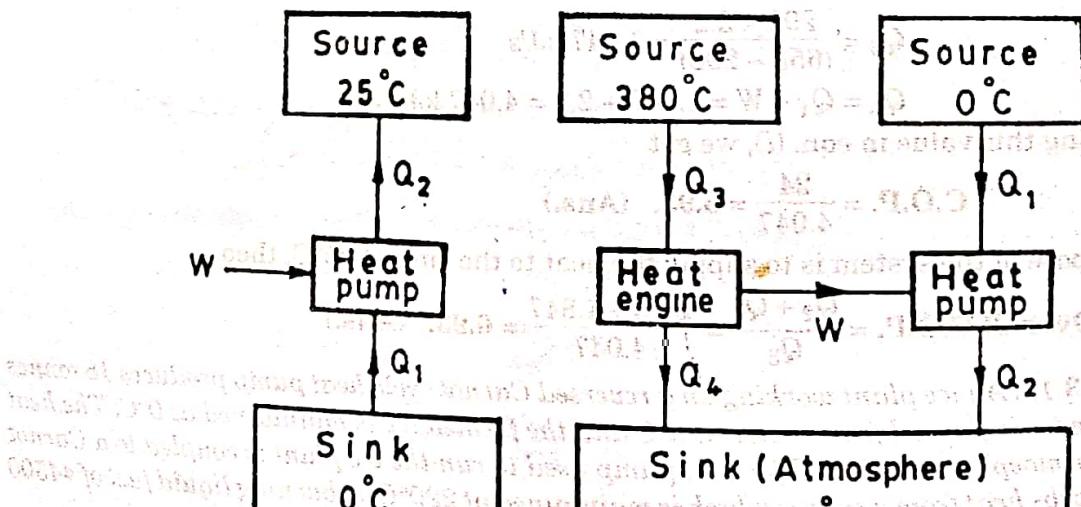
(ii) If the required input to run the pump is developed by a reversible engine which receives heat at 380°C and rejects heat to atmosphere, then determine the overall C.O.P. of the system.

(PTU, Jan. 2002)

Solution. Refer Fig. 3.15 (a).

(i) Temperature, $T_1 = 25 + 273 = 298 \text{ K}$

Temperature, $T_2 = 0 + 273 = 273 \text{ K}$



(a) Single system

(b) Combined system

Fig. 3.15

Heat removal rate from the refrigerator, $Q_1 = 1440 \text{ kJ/min} = 24 \text{ kJ/s}$
 Now, co-efficient of performance, for reversible heat pump,

$$(C.O.P.)_{\text{heat pump}} = \frac{T_1}{T_1 - T_2} = \frac{298}{(298 - 273)} = 11.92. \text{ (Ans.)}$$

$$\therefore (C.O.P.)_{\text{ref}} = \frac{T_2}{T_1 - T_2} = \frac{273}{298 - 273} = 10.92$$

Now, $10.92 = \frac{Q_1}{W} = \frac{24}{W}$

$\therefore W = 2.2 \text{ kW}$

i.e., **Work input required = 2.2 kW. (Ans.)**

$$Q_2 = Q_1 + W = 24 + 2.2 = 26.2 \text{ kJ/s}$$

(ii) Refer Fig. 3.15 (b).

The overall C.O.P. is given by,

$$C.O.P. = \frac{\text{heat removed from the refrigerator}}{\text{heat supplied from the source}}$$

$$= \frac{Q_1}{Q_3}$$

For the reversible engine, we can write

$$\frac{Q_3}{T_3} = \frac{Q_4}{T_4}$$

or

$$\frac{Q_4 + W}{T_3} = \frac{Q_4}{T_4}$$

or

$$\frac{Q_4 + 2.2}{(380 + 273)} = \frac{Q_4}{(25 + 273)}$$

or

$$\frac{Q_4 + 2.2}{653} = \frac{Q_4}{298}$$

or

$$298(Q_4 + 2.2) = 653 Q_4$$

or

$$Q_4(653 - 298) = 298 \times 2.2$$

or

$$Q_4 = \frac{298 \times 2.2}{(653 - 298)} = 1.847 \text{ kJ/s}$$

$\therefore Q_3 = Q_4 + W = 1.847 + 2.2 = 4.047 \text{ kJ/s}$

Substituting this value in eqn. (i), we get

$$C.O.P. = \frac{24}{4.047} = 5.93. \text{ (Ans.)}$$

If the purpose of the system is to supply the heat to the sink at 25°C , then

$$\text{Overall C.O.P.} = \frac{Q_2 + Q_4}{Q_3} = \frac{26.2 + 1.847}{4.047} = 6.93. \text{ (Ans.)}$$

Example 3.14. An ice plant working on a reversed Carnot cycle heat pump produces 15 tonnes of ice per day. The ice is formed from water at 0°C and the formed ice is maintained at 0°C . The heat is rejected to the atmosphere at 25°C . The heat pump used to run the ice plant is coupled to a Carnot engine which absorbs heat from a source which is maintained at 220°C by burning liquid fuel of 44500 kJ/kg calorific value and rejects the heat to the atmosphere. Determine :

(i) Power developed by the engine ;

(ii) Fuel consumed per hour.

Take enthalpy of fusion of ice = 334.5 kJ/kg .

Solution. Fig. 3.16 shows the arrangement of the system.

Amount of ice produced per day = 15 tonnes.

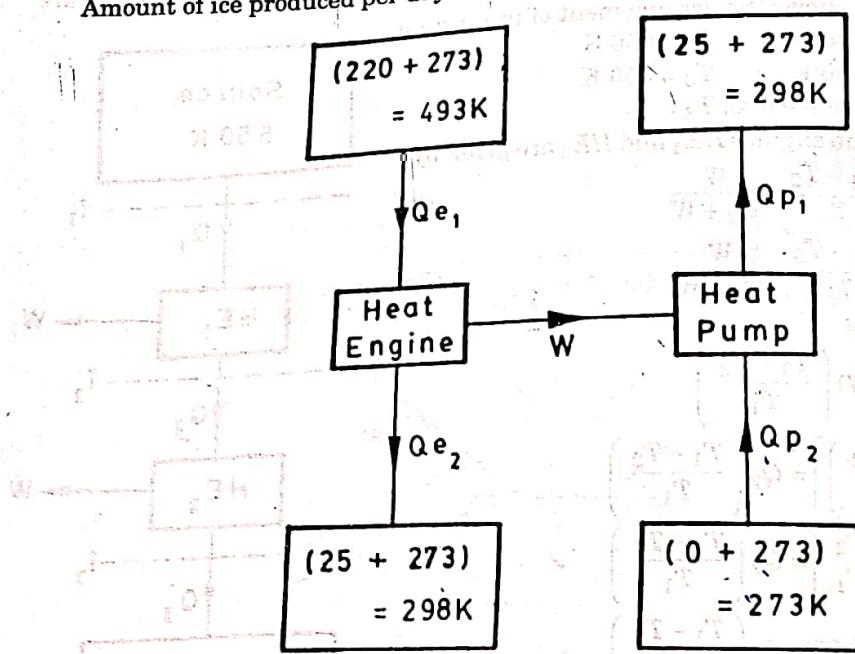


Fig. 3.16

∴ The amount of heat removed by the heat pump,

$$Q_{p2} = \frac{15 \times 1000 \times 334.5}{24 \times 60} = 3484.4 \text{ kJ/min}$$

$$\text{C.O.P. of the heat pump} = \frac{Q_{p2}}{W} = \frac{273}{298 - 273}$$

$$\therefore W = Q_{p2} \times \frac{298 - 273}{273} = 3484.4 \times \frac{25}{273} = 319.08 \text{ kJ/min}$$

This work must be developed by the Carnot engine,

$$W = \frac{319.08}{60} = 5.3 \text{ kJ/s} = 5.3 \text{ kW}$$

Thus power developed by the engine = 5.3 kW. (Ans.)

(ii) The efficiency of Carnot engine is given by

$$\eta_{\text{carnot}} = \frac{W}{Q_{e1}} = 1 - \frac{298}{493} = 0.396$$

$$\therefore Q_{e1} = \frac{W}{0.396} = \frac{5.3}{0.396} = 13.38 \text{ kJ/s}$$

$$\therefore Q_{e1} (\text{per hour}) = 13.38 \times 60 \times 60 = 48168 \text{ kJ}$$

∴ Quantity of fuel consumed/hour

$$= \frac{48168}{44500} = 1.082 \text{ kg/h. (Ans.)}$$

Example 3.15. Two Carnot engines work in series between the source and sink temperatures of 550 K and 350 K. If both engines develop equal power determine the intermediate temperature.

Solution. Fig. 3.17 shows the arrangement of the system.
Temperature of the source, $T_1 = 550 \text{ K}$

Temperature of the sink, $T_3 = 350 \text{ K}$

Intermediate temperature, T_2 :

The efficiencies of the engines HE_1 and HE_2 are given by

$$\eta_1 = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} = \frac{W}{Q_2 + W} \quad \dots(i)$$

$$\eta_2 = \frac{W}{Q_2} = \frac{T_2 - T_3}{T_2} = \frac{W}{Q_3 + W} \quad \dots(ii)$$

From eqn. (i), we get

$$W = (Q_2 + W) \left(\frac{T_1 - T_2}{T_1} \right)$$

$$\therefore W \left[1 - \left(\frac{T_1 - T_2}{T_1} \right) \right] = Q_2 \left(\frac{T_1 - T_2}{T_1} \right) \quad \dots(iii)$$

$$\therefore W \left(\frac{T_2}{T_1} \right) = Q_2 \left(\frac{T_1 - T_2}{T_1} \right)$$

$$\therefore W = Q_2 \left(\frac{T_1 - T_2}{T_2} \right) \quad \dots(iv)$$

From eqn. (ii), we get

$$W = Q_2 \left(\frac{T_2 - T_3}{T_2} \right) \quad \dots(v)$$

Now from eqns. (iii) and (iv), we get

$$T_1 - T_2 = T_2 - T_3$$

$$2T_2 = T_1 + T_3 = 550 + 350$$

$$\therefore T_2 = 450 \text{ K}$$

Hence intermediate temperature = 450 K. (Ans.)

Example 3.16. A Carnot heat engine draws heat from a reservoir at temperature T_1 and rejects heat to another reservoir at temperature T_3 . The Carnot forward cycle engine drives a Carnot reversed cycle engine or Carnot refrigerator which absorbs heat from reservoir at temperature T_3 and rejects heat to a reservoir at temperature T_2 . If the high temperature $T_1 = 600 \text{ K}$ and low temperature $T_2 = 300 \text{ K}$, determine :

(i) The temperature T_3 such that heat supplied to engine Q_1 is equal to the heat absorbed by refrigerator Q_2 .

(ii) The efficiency of Carnot engine and C.O.P. of Carnot refrigerator.

Solution. Refer Fig. 3.18.

Temperature, $T_1 = 600 \text{ K}$

Temperature, $T_2 = 300 \text{ K}$

Efficiency of Carnot engine,

$$\eta_{\text{carnot engine}} = \frac{Q_1 - Q_1'}{Q_1} = \frac{T_1 - T_3}{T_1}$$

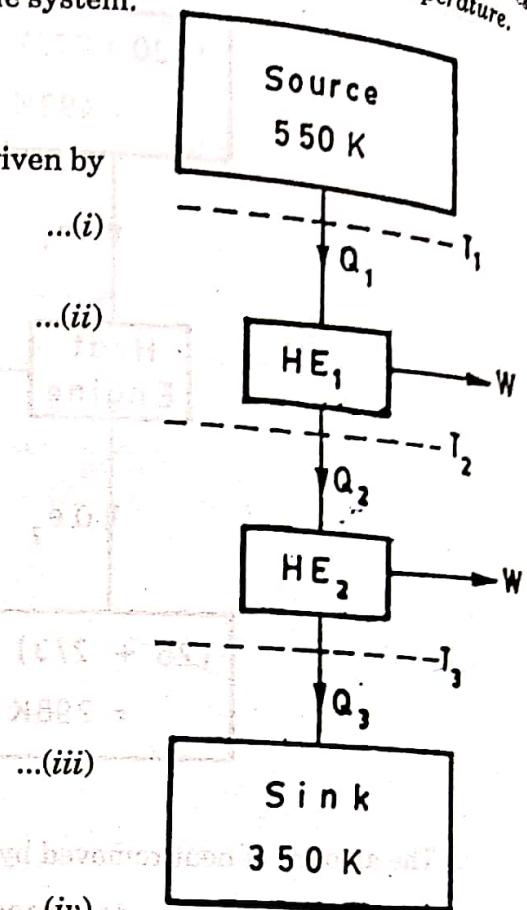


Fig. 3.17

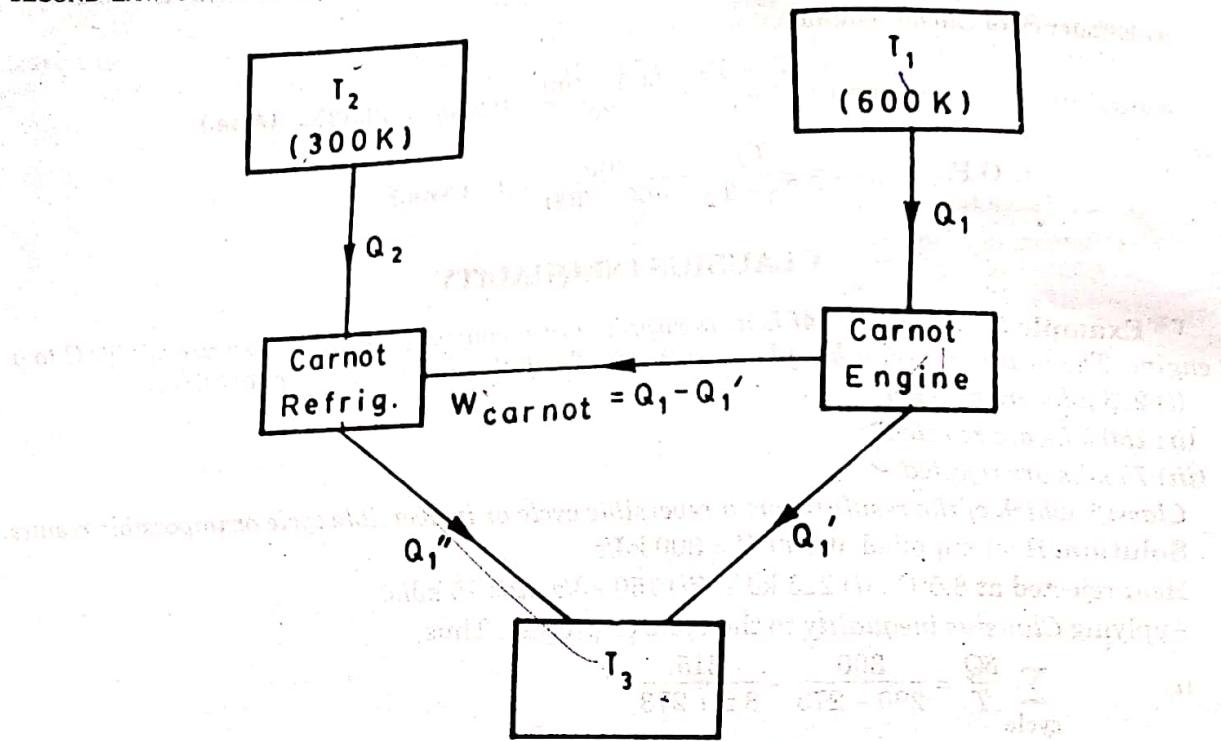


Fig. 3.18 Carnot refrigeration cycle

$$\text{Work of Carnot engine} = \frac{W_{\text{carnot}}}{\text{Heat supplied to the Carnot engine}} = \frac{W_{\text{carnot}}}{Q_1}$$

or

$$W_{\text{carnot}} = Q_1 \left(\frac{T_1 - T_3}{T_1} \right) \quad \dots(i)$$

$$\begin{aligned} \text{Also C.O.P. (carnot refrigerator)} &= \frac{Q_2}{Q_2 - Q_1} = \frac{T_2}{T_3 - T_2} \\ &= \frac{\text{Heat absorbed}}{W_{\text{carnot}}} = \frac{Q_2}{W_{\text{carnot}}} \end{aligned}$$

$$W_{\text{carnot}} = Q_2 \left(\frac{T_3 - T_2}{T_2} \right) \quad \dots(ii)$$

(i) Temperature, T_3 :

From eqns. (i) and (ii), we get

$$Q_1 \left(\frac{T_1 - T_3}{T_1} \right) = Q_2 \left(\frac{T_3 - T_2}{T_2} \right)$$

∴

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \left(\frac{T_1 - T_3}{T_3 - T_2} \right)$$

or

or

$$\frac{Q_2}{Q_1} = 1 = \frac{300}{600} \left(\frac{600 - T_3}{T_3 - 300} \right)$$

$$600 - T_3 = 2(T_3 - 300)$$

$$600 - T_3 = 2T_3 - 600 \quad \text{or} \quad T_3 = 400 \text{ K}$$

Hence, temperature, $T_3 = 400 \text{ K. (Ans.)}$

(ii) Efficiency of Carnot engine,

$$\eta_{\text{Carnot engine}} = \frac{T_1 - T_3}{T_1} = \frac{600 - 400}{600} = 0.3333 = 33.33\%. \quad (\text{Ans.})$$

$$\text{C.O.P.}_{\text{refrigerator}} = \frac{T_2}{T_3 - T_2} = \frac{300}{400 - 300} = 3. \quad (\text{Ans.})$$

CLAUSIUS INEQUALITY

~~Example 3.17.~~ 300 kJ/s of heat is supplied at a constant fixed temperature of 290°C to a heat engine. The heat rejection takes place at 8.5°C. The following results were obtained:

- (i) 215 kJ/s are rejected.
- (ii) 150 kJ/s are rejected.
- (iii) 75 kJ/s are rejected.

Classify which of the result report a reversible cycle or irreversible cycle or impossible results.

Solution. Heat supplied at 290°C = 300 kJ/s

Heat rejected at 8.5°C : (i) 215 kJ/s, (ii) 150 kJ/s, (iii) 75 kJ/s.

Applying Clausius inequality to the cycle or process. Thus,

$$(i) \sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{300}{290 + 273} - \frac{215}{8.5 + 273} \\ = 0.5328 - 0.7637 = -0.2309 < 0.$$

∴ Cycle is irreversible. (Ans.)

$$(ii) \sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{300}{290 + 273} - \frac{150}{8.5 + 273} \\ = 0.5328 - 0.5328 = 0$$

∴ Cycle is reversible. (Ans.)

$$(iii) \sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{300}{290 + 273} - \frac{75}{8.5 + 273} \\ = 0.5328 - 0.2664 = 0.2664 > 0.$$

This cycle is impossible by second law of thermodynamics, i.e. Clausius inequality. (Ans.)

Example 3.18. A steam power plant operates between boiler temperature of 160°C and condenser temperature of 50°C. Water enters the boiler as saturated liquid and steam leaves the boiler as saturated vapour. Verify the Clausius inequality for the cycle.

Given : Enthalpy of water entering boiler = 687 kJ/kg.

Enthalpy of steam leaving boiler = 2760 kJ/kg

Condenser pressure = $0.124 \times 10^5 \text{ N/m}^2$.

Solution. Boiler temperature, $T_1 = 160 + 273 = 433 \text{ K}$

Condenser temperature, $T_2 = 50 + 273 = 323 \text{ K}$

From steam tables :

Enthalpy of water entering boiler, $h_{f1} = 687 \text{ kJ/kg}$

Enthalpy of steam leaving boiler, $h_2 = 2760 \text{ kJ/kg}$

Condenser pressure = $0.124 \times 10^5 \text{ N/m}^2$

Boiler pressure = $6.18 \times 10^5 \text{ N/m}^2$ (corresponding to 160°C)

Enthalpy of vapour leaving the turbine, $h_3 = 2160 \text{ kJ/kg}$

(assuming isentropic expansion)

If the cycle is reversible between the same temperature limits and the heat supplied at higher temperature is same, the heat rejected can be calculated as follows :

$$\eta_{\text{reversible}} = 1 - \frac{T_2}{T_1} = 1 - \frac{324}{437} = 0.2586 \text{ or } 25.86\%$$

∴ Heat rejected per kg is given by

$$Q_2 = (1 - 0.2586) \times Q_1 = (1 - 0.2586) \times 2070 = 1534.7 \text{ kJ/kg}$$

$$\sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{2070}{437} - \frac{1534.7}{324} = 4.73 - 4.73 = 0$$

i.e.,

$$\sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{Q_{\text{added}}}{T_{\text{source}}} - \frac{Q_{\text{rejected}}}{T_{\text{sink}}} = 0$$

Thus Clausius Equality sign for a reversible engine is verified.

3.12. ENTROPY

3.12.1. Introduction

In heat engine theory, the term entropy plays a vital role and leads to important results which by other methods can be obtained much more laboriously.

It may be noted that all heat is not equally valuable for converting into work. Heat that is supplied to a substance at high temperature has a greater possibility of conversion into work than heat supplied to a substance at a lower temperature.

"Entropy is a function of a quantity of heat which shows the possibility of conversion of that heat into work. The increase in entropy is small when heat is added at a high temperature and is greater when heat addition is made at a lower temperature. Thus for maximum entropy, there is minimum availability for conversion into work and for minimum entropy there is maximum availability for conversion into work."

3.12.2. Entropy—a Property of a System

Refer Fig. 3.20. Let us consider a system undergoing a reversible process from state 1 to state 2 along path L and then from state 2 to the original state 1 along path M. Applying the Clausius theorem to this reversible cyclic process, we have

$$\oint_R \frac{\delta Q}{T} = 0$$

(where the subscript designates a reversible cycle)

Hence when the system passes through the cycle 1-L-2-M-1, we have

$$\int_{1(L)}^2 \frac{\delta Q}{T} + \int_{2(M)}^1 \frac{\delta Q}{T} = 0 \quad \dots(3.16)$$

Now consider another reversible cycle in which the system changes from state 1 to state 2 along path L, but returns from state 2 to the original state 1 along a different path N. For this reversible cyclic process, we have

$$\int_{1(L)}^2 \frac{\delta Q}{T} + \int_{2(N)}^1 \frac{\delta Q}{T} = 0 \quad \dots(3.17)$$

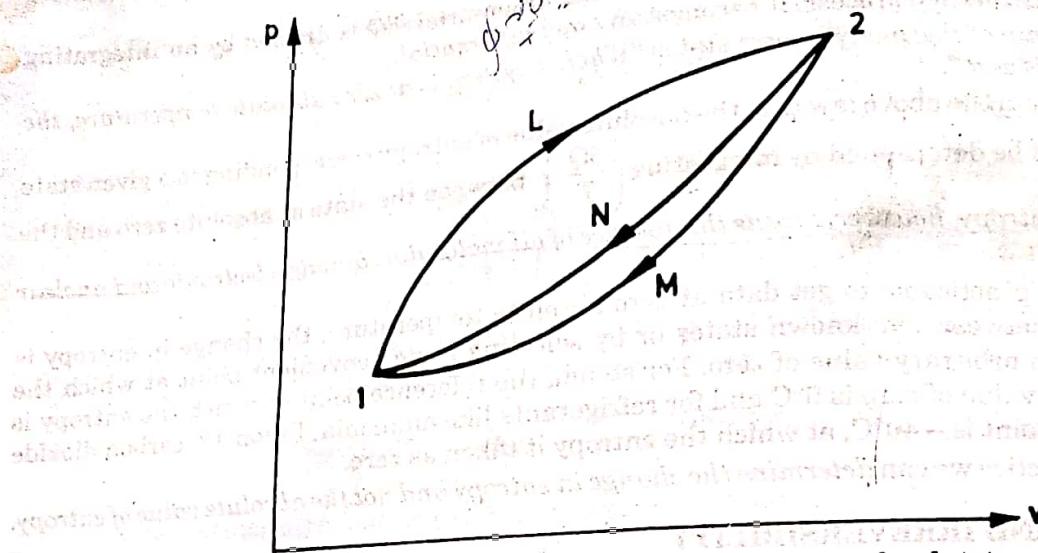


Fig. 3.20. Reversible cyclic process between two fixed end states.

Subtracting equation (3.17) from equation (3.16), we have

$$\int_{2(M)}^1 \frac{\delta Q}{T} - \int_{2(N)}^1 \frac{\delta Q}{T} = 0$$

$$\text{or } \int_1^{2(M)} \frac{\delta Q}{T} = \int_1^{2(N)} \frac{\delta Q}{T}$$

As no restriction is imposed on paths L and M , except that they must be reversible, the quantity $\frac{\delta Q}{T}$ is a function of the initial and final states of the system and is independent of the path of the process. Hence it represents a property of the system. This property is known as the "entropy".

3.12.3. Change of Entropy in a Reversible Process

Refer Fig. 3.20.

Let S_1 = entropy at the initial state 1, and

S_2 = entropy at the final state 2.

Then, the change in entropy of a system, as it undergoes a change from state 1 to 2, becomes

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_R \quad \dots(3.18)$$

Lastly, if the two equilibrium states 1 and 2 are infinitesimal near to each other, the integral sign may be omitted and $S_2 - S_1$ becomes equal to dS .

Hence equation (3.18) may be written as

$$dS = \left(\frac{\delta Q}{T} \right)_R \quad \dots(3.19)$$

where dS is an exact differential.

Thus, from equation (3.19), we find that the change of entropy in a reversible process is equal to $\frac{\delta Q}{T}$. This is the mathematical formulation of the second law of thermodynamics.

Equation (3.19) indicates that when an *inexact differential* δQ is divided by an integrating factor T during a reversible process, it becomes an *exact differential*.

The *third law of thermodynamics* states "When a system is at zero absolute temperature, the entropy of system is zero".

It is clear from the above law that the absolute value of entropy corresponding to a given state of the system could be determined by integrating $\left(\frac{\delta Q}{T}\right)_R$ between the state at absolute zero and the given state. Zero entropy, however, means the absence of all molecular, atomic, electronic and nuclear disorders.

As it is not practicable to get data at zero absolute temperature, the change in entropy is calculated either between two known states or by selecting some convenient point at which the entropy is given an arbitrary value of zero. For steam, the reference point at which the entropy is given an arbitrary value of zero is 0°C and for refrigerants like ammonia, Freon-12, carbon dioxide etc. the reference point is -40°C , at which the entropy is taken as zero.

Thus, in practice we can determine the change in entropy and not the absolute value of entropy.

3.13. ENTROPY AND IRREVERSIBILITY

We know that change in entropy in a *reversible process* is equal to $\left(\frac{\delta Q}{T}\right)_R$ (equation 3.19). Let us now find the change in entropy in an *irreversible process*.

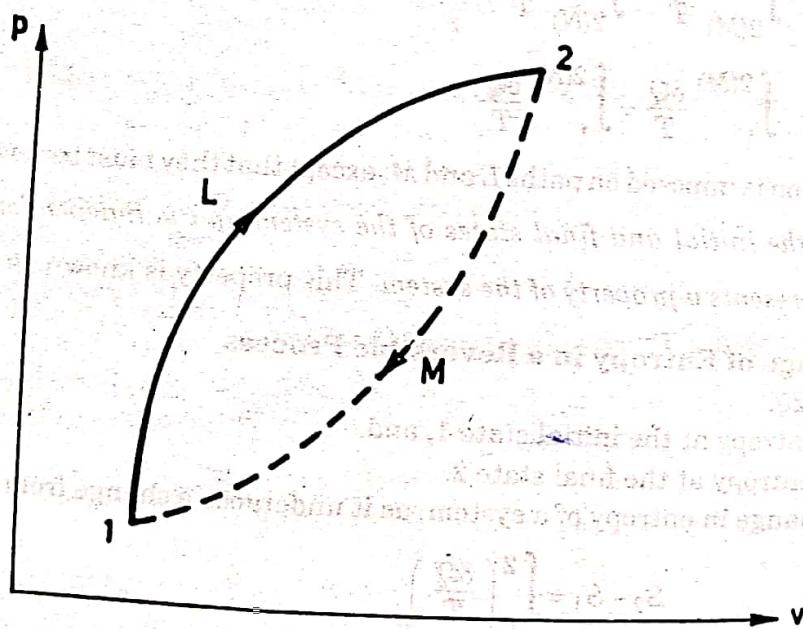


Fig. 3.21. Entropy change for an irreversible process.

Consider a closed system undergoing a change from state 1 to state 2 by a reversible process 1-L-2 and returns from state 2 to the initial state 1 by an irreversible process 2-M-1 as shown in Fig. 3.21 on the thermodynamic coordinates, pressure and volume.

Since entropy is a thermodynamic property, we can write

$$\oint dS = \int_{1(L)}^2 (dS)_R + \int_{2(M)}^1 (dS)_I = 0 \quad \dots(3.20)$$

(Subscript I represents the irreversible process).

SECOND LAW OF THERMODYNAMICS AND ENTROPY

Now for a reversible process, from equation (3.19), we have

$$\int_{1(L)}^2 (dS)_R = \int_{1(L)}^2 \left(\frac{\delta Q}{T} \right)_R \quad \dots(3.21)$$

Substituting the value of $\int_{1(L)}^2 (dS)_R$ in equation (3.20), we get

$$\int_{1(L)}^2 \left(\frac{\delta Q}{T} \right)_R + \int_{2(M)}^1 (dS)_I = 0 \quad \dots(3.22)$$

Again, since in equation (3.20) the processes 1-L-2 and 2-M-1 together form an irreversible cycle, applying Clausius equality to this expression, we get

$$\oint \frac{\delta Q}{T} = \int_{1(L)}^2 \left(\frac{\delta Q}{T} \right)_R + \int_{2(M)}^1 \left(\frac{\delta Q}{T} \right)_I < 0 \quad \dots(3.23)$$

Now subtracting equation (3.23) from equation (3.22), we get

$$\int_{2(M)}^1 (dS)_I > \int_{2(M)}^1 \left(\frac{\delta Q}{T} \right)_I \quad \checkmark$$

which for infinitesimal changes in states can be written as

$$(dS)_I > \int \left(\frac{\delta Q}{T} \right)_I \quad \dots(3.24)$$

Equation (3.24) states that the *change in entropy in an irreversible process is greater than* $\frac{\delta Q}{T}$.

Combining equations (3.23) and (3.24), we can write the equation in the general form as

$$dS \geq \frac{\delta Q}{T} \quad \dots(3.25)$$

where *equality sign stands for the reversible process and inequality sign stands for the irreversible process.*

It may be noted here that the effect of irreversibility is always to increase the entropy of the system.

Let us now consider an *isolated system*. We know that in an isolated system, matter, work or heat cannot cross the boundary of the system. Hence according to first law of thermodynamics, the internal energy of the system will remain constant.

Since for an isolated system, $\delta Q = 0$, from equation (3.25), we get

$$(dS)_{\text{isolated}} \geq 0 \quad \dots(3.26)$$

Equation (3.26) states that the *entropy of an isolated system either increases or remains constant*. This is a corollary of the second law. It explains the *principle of increase in entropy*.

3.14. CHANGE IN ENTROPY OF THE UNIVERSE

We know that the entropy of an isolated system either increase or remains constant, i.e.

$$(dS)_{\text{isolated}} \geq 0$$

By including any system and its surrounding within a single boundary, as shown in Fig. 3.22, an isolated system can be formed. The combination of the system and the surroundings within a

If the process is reversible adiabatic, then

$$\sum s \cdot \dot{m} = 0.$$

...(3.41)

ENTROPY

Example 3.20. An iron cube at a temperature of 400°C is dropped into an insulated bath containing 10 kg water at 25°C . The water finally reaches a temperature of 50°C at steady state. Given that the specific heat of water is equal to $4186 \text{ J/kg}\cdot\text{K}$. Find the entropy changes for the iron cube and the water. Is the process reversible? If so why? (GATE 1996)

Solution. Given : Temperature of iron cube = $400^{\circ}\text{C} = 673 \text{ K}$

Temperature of water = $25^{\circ}\text{C} = 298 \text{ K}$

Mass of water = 10 kg

Temperature of water and cube after equilibrium = $50^{\circ}\text{C} = 323 \text{ K}$

Specific heat of water, $c_{pw} = 4186 \text{ J/kg K}$

Entropy changes for the iron cube and the water :

Is the process reversible?

Now, heat lost by iron cube = heat gained by water

$$\begin{aligned} m_i c_{pi} (673 - 323) &= m_w c_{pw} (323 - 298) \\ &= 10 \times 4186 (323 - 298) \\ m_i c_{pi} &= \frac{10 \times 4186 (323 - 298)}{(673 - 323)} = 2990 \end{aligned}$$

where m_i = mass of iron, kg ;

c_{pi} = specific heat of iron, J/kg K

Entropy of iron at 673 K

$$= m_i c_{pi} \ln \left(\frac{673}{273} \right) = 2990 \ln \left(\frac{673}{273} \right)$$

$$= 2697.8 \text{ J/K}$$

Entropy of water at 298 K

$$= m_w c_{pw} \ln \left(\frac{298}{273} \right)$$

$$= 10 \times 4186 \ln \left(\frac{298}{273} \right) = 3667.8 \text{ J/K}$$

[Taking 0°C as datum]

Entropy of iron at 323 K

$$= 2990 \times \ln \left(\frac{323}{273} \right) = 502.8 \text{ J/K}$$

Entropy water at 323 K

$$= 10 \times 4186 \ln \left(\frac{323}{273} \right) = 7040.04 \text{ J/K}$$

Change in entropy of iron

$$= 502.8 - 2697.8 = -2195 \text{ J/K}$$

Change in entropy of water

$$= 7040.04 - 3667.8 = 3372.24 \text{ J/K}$$

Net change in entropy

$$= 3372.24 - 2195 = 1177.24 \text{ J/K}$$

Since $\Delta S > 0$ hence the process is irreversible. Ans.

Example 3.21. An ideal gas is heated from temperature T_1 to T_2 by keeping its volume constant. The gas is expanded back to its initial temperature according to the law $pv^n = \text{constant}$. If the entropy changes in the two processes are equal, find the value of n in terms of the adiabatic index γ .

Solution. Change in entropy during constant volume process (U.P.S.C. 1997)

$$= mc_v \ln \left(\frac{T_2}{T_1} \right) \quad \dots(i)$$

Change in entropy during polytropic process ($pv^n = \text{constant}$)

$$= mc_v \left(\frac{\gamma - n}{n - 1} \right) \ln \left(\frac{T_2}{T_1} \right) \quad \dots(ii)$$

For the same entropy, equating (i) and (ii), we have

$$\frac{\gamma - n}{n - 1} = 1 \quad \text{or} \quad (\gamma - n) = (n - 1) \quad \text{or} \quad 2n = \gamma + 1$$

∴

$$n = \frac{\gamma + 1}{2} \quad \text{Ans.}$$

3.19. THE THIRD LAW OF THERMODYNAMICS

The third law of thermodynamics is stated as follows :

"The entropy of all perfect crystalline solids is zero at absolute zero temperature".

- The third law of thermodynamics, often referred to as **Nernst law**, provides the basis for the calculation of absolute entropies of substances.

According to this law, if the entropy is zero at $T = 0$, the absolute entropy s_{ab} of a substance at any temperature T and pressure p is expressed by the expression

$$s_{ab.} = \int_0^{T_s} T_s c_{ps} \frac{dT}{T} + \frac{h_{sf}}{T_s} + \int_{T_s}^{T_f2} T_g c_{pf} \frac{dT}{T} + \frac{h_{fg}}{T_g} \int_{T_g}^T c_{pg} \frac{dT}{T} \quad \dots(3.16)$$

where

$$T_s = T_{f1} = T_{sf} = T_{sat} \dots \text{for fusion,}$$

$$T_{f2} = T_g = T_{fg} = T_{sat} \dots \text{for vaporisation}$$

c_{ps}, c_{pf}, c_{pg} = constant pressure specific heats for solids, liquids and gas,

h_{sf}, h_{fg} = latent heats of fusion and vaporisation.

Thus by putting $s = 0$ at $T = 0$, one may integrate zero kelvin and standard state of 298.15 K and 1 atm., and find the entropy difference.

Further, it can be shown that the entropy of a crystalline substance at $T = 0$ is not a function of pressure, viz., $\left(\frac{\partial s}{\partial p}\right)_{T=0} = 0$

However, at temperatures above absolute zero, the entropy is a function of pressure also. The absolute entropy of a substance at 1 atm pressure can be calculated using eqn. (3.16); for pressures different from 1 atm, necessary corrections have to be applied.

Example 3.22. Air at 20°C and 1.05 bar occupies 0.025 m^3 . The air is heated at constant volume until the pressure is 4.5 bar, and then cooled at constant pressure back to original temperature. Calculate :

(i) The net heat flow from the air.

(ii) The net entropy change.

Sketch the process on T-s diagram.

Solution. The processes are shown on a T-s diagram in Fig. 3.30.

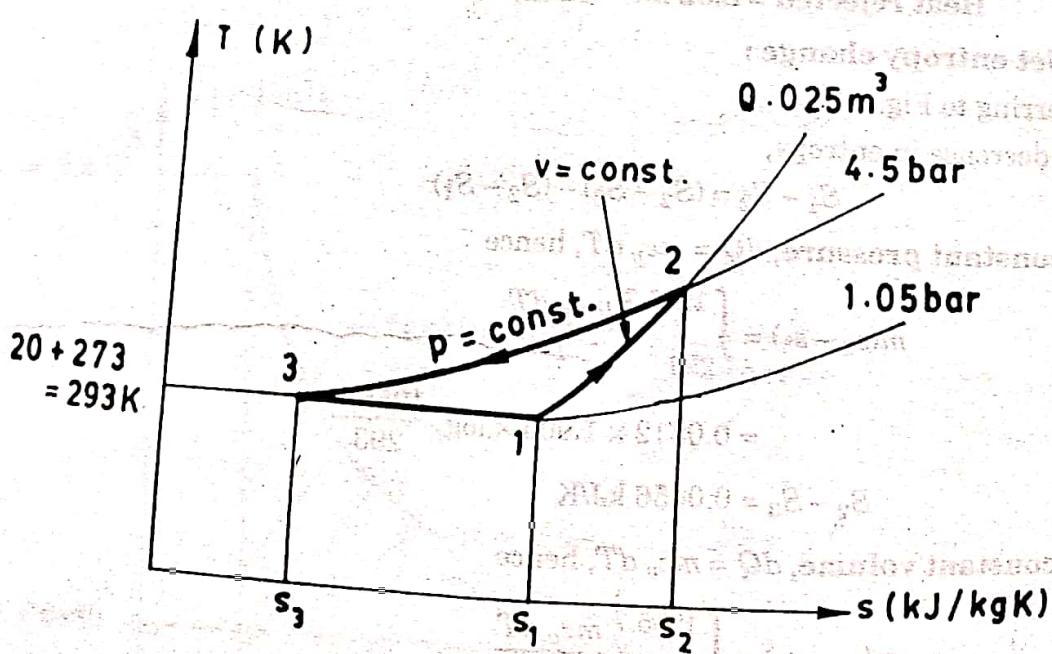


Fig. 3.30

For air :

Temperature,

$$T_1 = 20 + 273 = 293 \text{ K}$$

Volume,

$$V_1 = V_3 = 0.025 \text{ m}^3$$

Pressure,

$$p_1 = 1.05 \text{ bar} = 1.05 \times 10^5 \text{ N/m}^2$$

Pressure,

$$p_2 = 4.5 \text{ bar} = 4.5 \times 10^5 \text{ N/m}^2$$

(i) Net heat flow :

For a perfect gas (corresponding to point 1 of air),

$$m = \frac{p_1 V_1}{RT_1} = \frac{1.05 \times 10^5 \times 0.025}{0.287 \times 10^3 \times 293} = 0.0312 \text{ kg}$$

For a perfect gas at *constant volume*,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

$$\frac{1.05}{293} = \frac{4.5}{T_2} \text{ or } T_2 = \frac{4.5 \times 293}{1.05} = 1255.7 \text{ K}$$

At **constant volume**,

$$Q = mc_v(T_2 - T_1) = 0.0312 \times 0.718(1255.7 - 293)$$

i.e.,

$$Q_{1-2} = 21.56 \text{ kJ.}$$

Also, at **constant pressure**,

$$Q = m \times c_p \times (T_3 - T_2) = 0.0312 \times 1.005(293 - 1255.7)$$

i.e.,

$$Q_{2-3} = -30.18 \text{ kJ}$$

∴ **Net heat flow** = $Q_{1-2} + Q_{2-3} = 21.56 + (-30.18) = -8.62 \text{ kJ}$

i.e.,

Heat rejected = 8.62 kJ. (Ans.)

(ii) Net entropy change :

Referring to Fig. 3.30.

Net decrease in entropy,

$$S_1 - S_2 = (S_2 - S_3) - (S_2 - S_1)$$

At **constant pressure**, $dQ = mc_p dT$, hence

$$\begin{aligned} m(s_2 - s_3) &= \int_{293}^{1255.7} \frac{mc_p}{T} dT \\ &= 0.0312 \times 1.005 \times \log_e \frac{1255.7}{293} \end{aligned}$$

i.e.,

$$S_2 - S_3 = 0.0456 \text{ kJ/K}$$

At **constant volume**, $dQ = mc_v dT$, hence

$$\begin{aligned} m(s_2 - s_1) &= \int_{293}^{1255.7} \frac{mc_v}{T} dT \\ &= 0.0312 \times 0.718 \times \log_e \frac{1255.7}{293} = 0.0326 \text{ kJ/K} \end{aligned}$$

i.e.,

$$S_2 - S_1 = 0.0326 \text{ kJ/K}$$

Isothermal $\rightarrow \frac{m}{T}$ const.

classmate

SECOND LAW OF THERMODYNAMICS AND ENTROPY

$$m(s_1 - s_3) = S_1 - S_3 = (S_2 - S_3) - (S_2 - S_1)$$
$$= 0.0456 - 0.0326 = 0.013 \text{ kJ/K}$$

Hence, decrease in entropy = 0.013 kJ/K. (Ans.)

Note that since entropy is a property, the decrease in entropy is given by $S_1 - S_3$, is independent of the process undergone between states 1 and 3.

Example 3.23. 0.04 m³ of nitrogen contained in a cylinder behind a piston is initially at 1.05 bar and 15°C. The gas is compressed isothermally and reversibly until the pressure is 4.8 bar. Calculate:

- The change of entropy;
- The heat flow;
- The work done;

Sketch the process on a p-v and T-s diagram.

Assume nitrogen to act as a perfect gas. Molecular weight of nitrogen = 28.

Solution. Refer Fig. 3.31.

Initial pressure, $p_1 = 1.05 \text{ bar} = 1.05 \times 10^5 \text{ N/m}^2$

Initial volume, $V_1 = 0.04 \text{ m}^3$

Temperature, $T_1 = 15 + 273 = 288 \text{ K}$

Final pressure, $p_2 = 4.8 \text{ bar} = 4.8 \times 10^5 \text{ N/m}^2$

Final temperature, $T_2 = T_1 = 288 \text{ K}$

The process is shown on a p-v and a T-s diagram in Fig. 3.31 (a) and 3.31 (b) respectively. The shaded area in Fig. 3.31 (a) represents work input, and the shaded area on Fig. 3.31 (b) represents heat rejected.

Characteristic gas constant,

$$R = \frac{\text{Universal gas constant, } R_0 = 8314}{\text{Molecular weight, } M = 28} = 297 \text{ Nm/kg K}$$

