When a system existing in mechanical and chemical equilibrium is separated from its surroundings by a diathermic wall (diathermic means 'which allows heat to flow') and if there is no spontaneous change in any property of the system, the system is said to exist in a state of *thermal equilibrium*. When this is not satisfied, the system will undergo a change of state till thermal equilibrium is restored.

When the conditions for any one of the three types of equilibrium are not satisfied, a system is said to be in a *nonequilibrium state*. If the nonequilibrium of the state is due to an unbalanced force in the interior of a system or between the system and the surroundings, the pressure varies from one part of the system to another. There is no single pressure that refers to the system as a whole. Similarly, if the nonequilibrium is because of the temperature of the system being different from that of its surroundings, there is a nonuniform temperature distribution set up within the system and there is no single temperature that stands for the system as a whole. It can thus be inferred that when the conditions for thermodynamic equilibrium are not satisfied, the states passed through by a system cannot be described by thermodynamic properties which represent the system as a whole.

Thermodynamic properties are the macroscopic coordinates defined for, and significant to, only thermodynamic equilibrium states. Both classical and statistical thermodynamics study mainly the equilibrium states of a system.

1.11   QUASI-STATIC PROCESS

Let us consider a system of gas contained in a cylinder (Fig. 1.13). The system initially is in an equilibrium state, represented by the properties p_1, v_1, t_1. The weight on the piston just balances the upward force exerted by the gas. If the weight is removed, there will be an unbalanced force between the system and the surroundings, and under gas pressure, the piston will move up till it hits the stops. The system again comes to an equilibrium state, being described by the properties p_2, v_2, t_2. But the intermediate states passed through by the system are nonequilibrium states which cannot be described by thermodynamic coordinates.
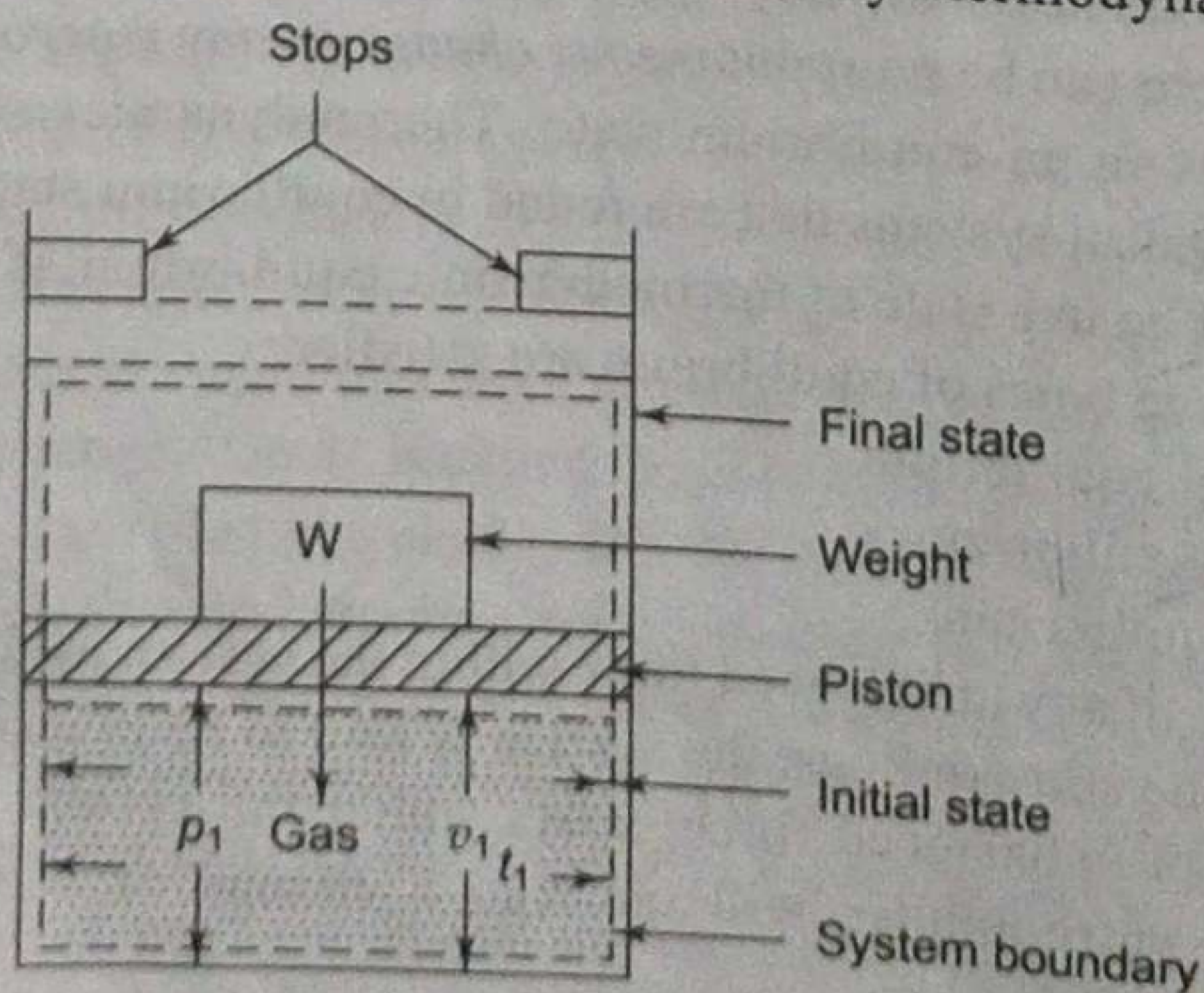

Fig. 1.13   *Transition between Two Equilibrium States by an Unbalanced Force*

Figure 1.14 shows points 1 and 2 as the initial and final equilibrium states joined by a dotted line, which has got no meaning otherwise. Now if the single weight on the piston is made up of many very small pieces of weights (Fig. 1.15), and these weights are removed one by one very slowly from the top of the piston, at any instant of the upward travel of the piston, if the gas system is isolated, *the departure of the state of the system from the thermodynamic equilibrium state will be infinitesimally small.* So every state passed through by the system will be an
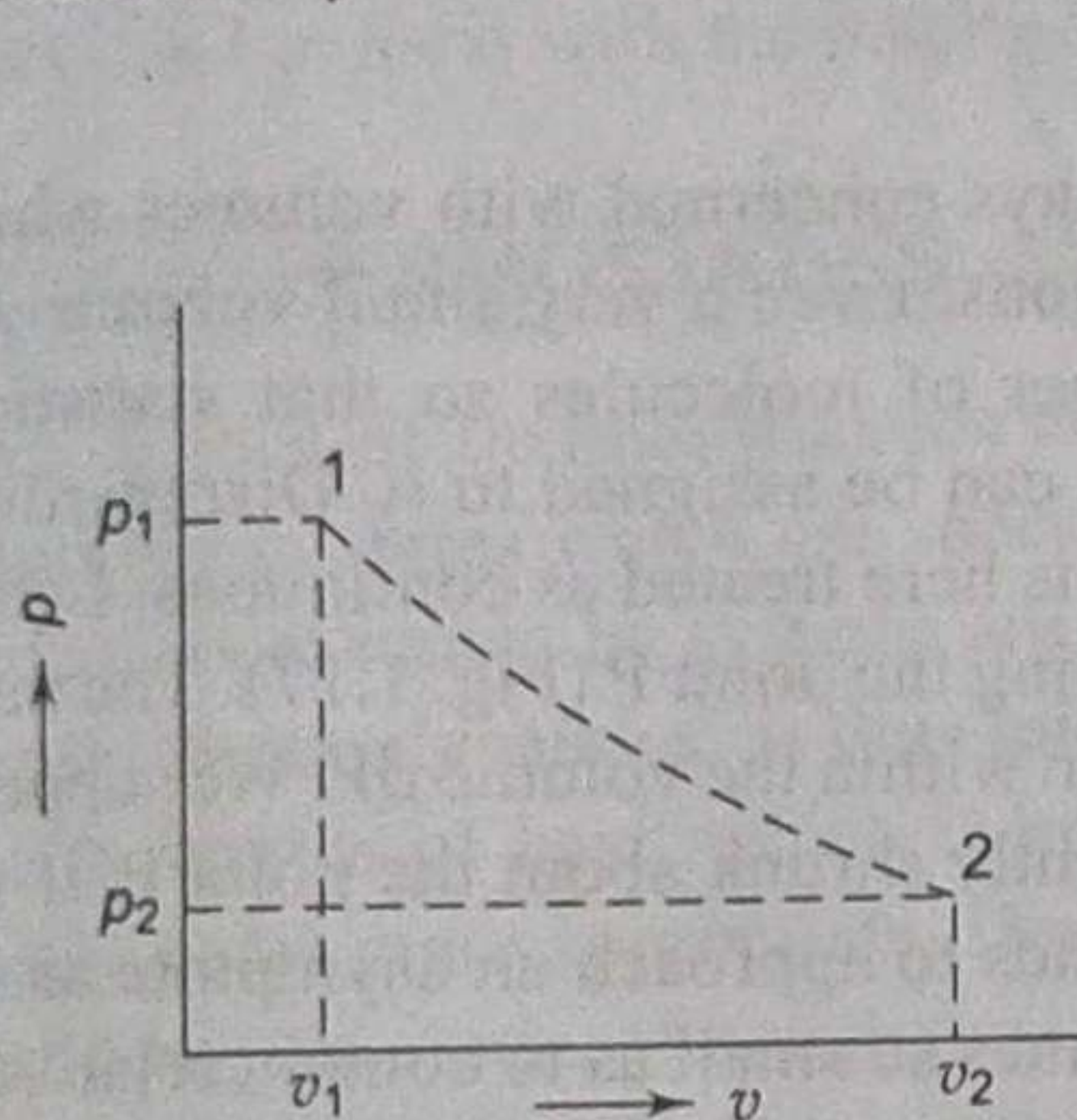

Fig. 1.14 *Plot Representing the Transition between Two Equilibrium States*
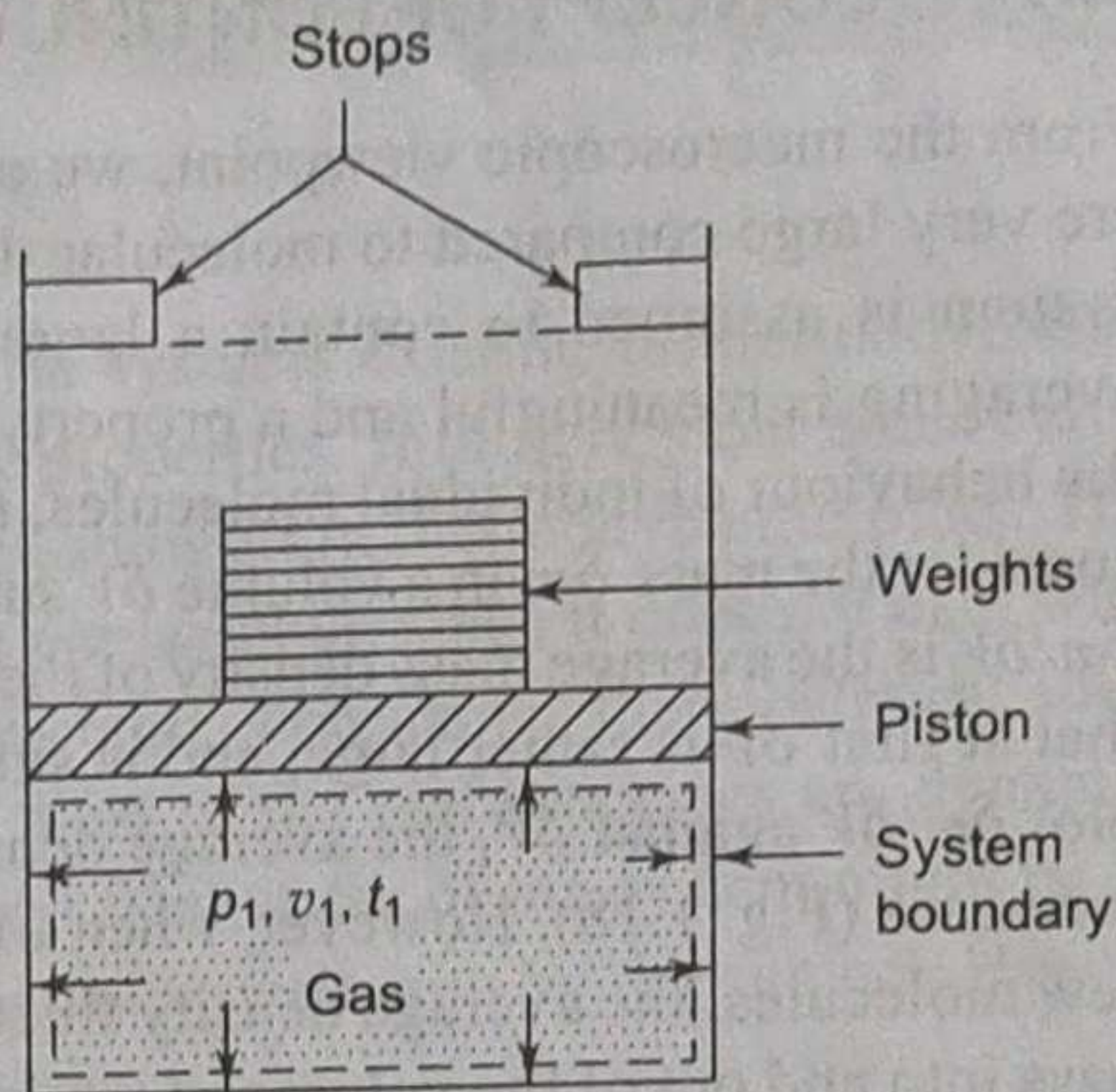

Fig. 1.15 *Infinitely Slow Transition of a System by Infinitesimal Force*

equilibrium state. Such a process, which is but a locus of all the equilibrium points passed through by the system, is known as a *quasi-static process* (Fig. 1.16), 'quasi' meaning 'almost'. *Infinite slowness is the characteristic feature of a quasi-static process.* A quasi-static process is thus a succession of equilibrium states. A quasi-static process is also called a *reversible process.*

1.12 PURE SUBSTANCE

A pure substance is defined as one that is homogeneous and invariable in chemical composition throughout its mass. The relative proportions of the chemical elements constituting the substance are also constant. Atmospheric air, steam-water mixture and combustion products of a fuel are regarded as pure substances. But the mixture of air and liquid air is not a pure substance, since the relative proportions of oxygen and nitrogen differ in the gas and liquid phases in equilibrium.
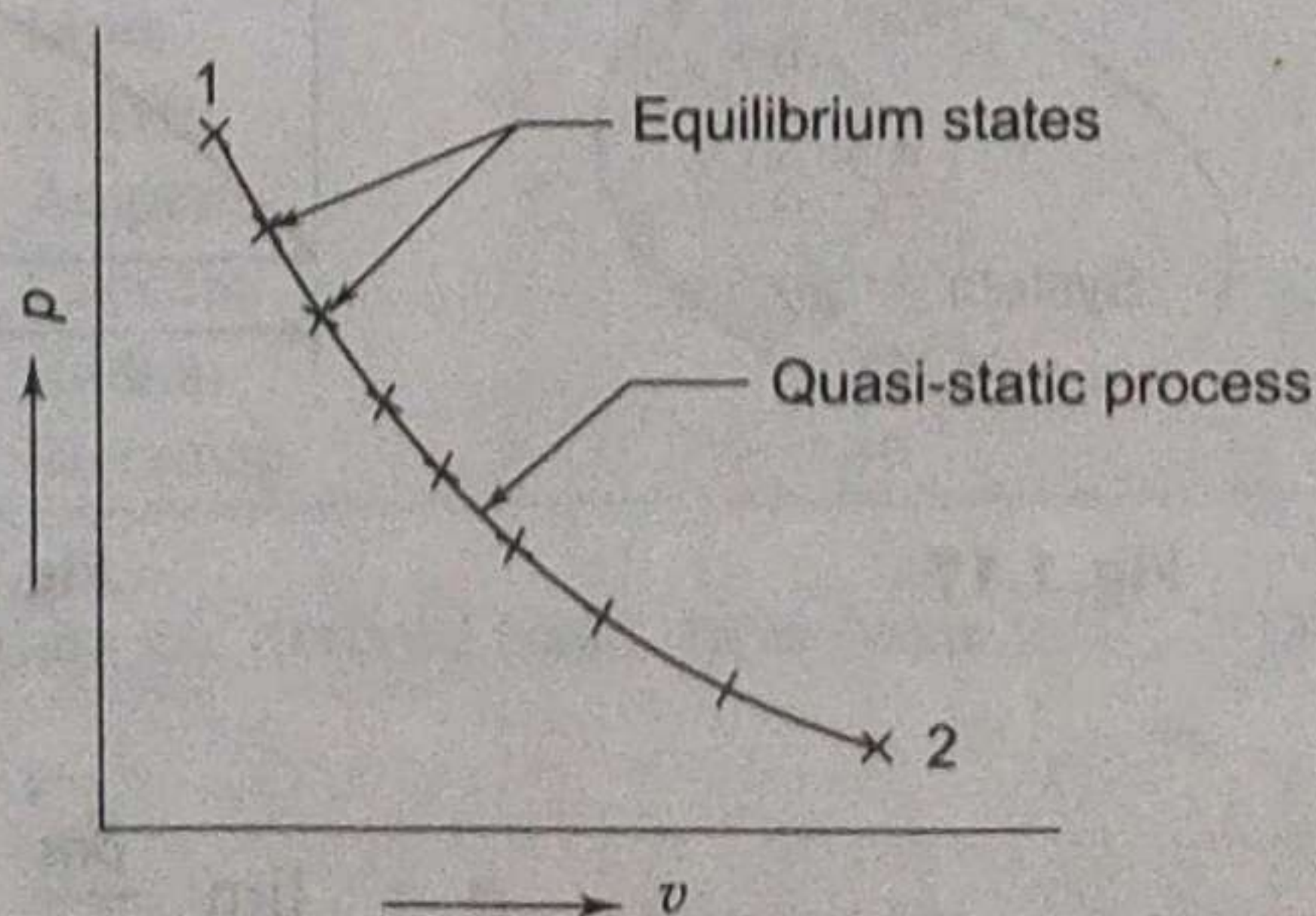

Fig. 1.16 *A Quasi-Static Process*

2.4 IDEAL GAS

It has been established from experimental observations that the $p - v - T$ behaviour of gases at a low pressure is closely given by the following relation

$$p\bar{v} = \bar{R}T \tag{2.6}$$

where $\bar{R}$ is the universal gas constant, 8.3143 J/mol K and $\bar{v}$ is the molar specific volume, m^3/gmol. (see Sec. 10.3.). Dividing Eq. (2.6) by the molecular weight μ,

$$pv = RT \tag{2.7}$$

where v is specific volume, in m^3/kg, and R is the characteristic gas constant. Substituting $R = \bar{R}/\mu$ J/kg K, we get in terms of the total volume V of gas,

$$PV = n\bar{R}T$$

$$PV = mRT \tag{2.8}$$

$$R = \frac{\bar{R}}{M\omega}$$

where n is the number of moles and m is the mass of the gas. Equation (2.8) can be written for two states of the gas,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{2.9}$$

Equation (2.6), (2.7) or (2.8) is called the *ideal gas equation of state*. At very low pressure or density, all gases and vapours approach ideal gas behaviour.

2.5 GAS THERMOMETERS

A schematic diagram of a constant volume gas thermometer is given in Fig. 2.1. A small amount of gas is enclosed in bulb B which is in communication via the capillary tube C with one limb of the mercury manometer M. The other limb of the mercury manometer is open to the atmosphere and can be moved vertically to adjust the mercury levels so that the mercury just touches lip L of the capillary. The pressure in the bulb is used as a thermometric property and is given by

$$p = p_0 + \rho_M Zg$$

where p_0 is the atmospheric pressure, ρ_M is the density of mercury.

When the bulb is brought in contact with the system whose temperature is to be measured, the bulb, in course of time, comes in thermal equilibrium with the system.

The gas in the bulb expands, on being heated, pushing the mercury downward. The flexible limb of the manometer is then adjusted so that the mercury again touches the lip L. The difference in mercury level Z is recorded and the pressure p of the gas in the bulb is estimated. Since the volume of the trapped gas is constant, from the ideal gas equation,

$$\Delta T = \frac{V}{R}\Delta p \qquad (2.10)$$

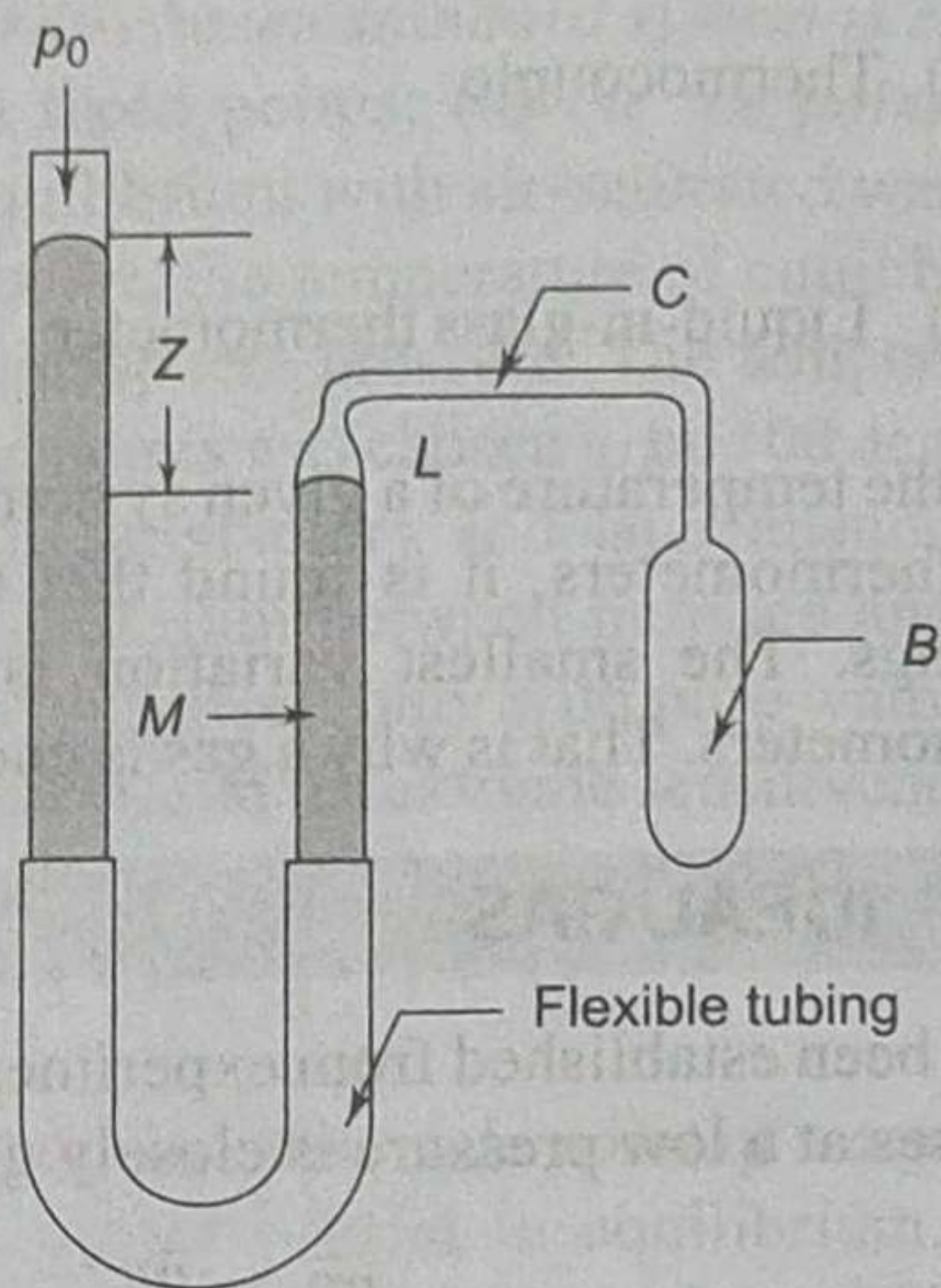i.e. the temperature increase is proportional to the pressure increase.

Fig. 2.1   Constant Volume Gas Thermometer

In a constant pressure gas thermometer, the mercury levels have to be adjusted to keep Z constant, and the volume of gas V, which would vary with the temperature of the system, becomes the thermometric property.

∴
$$\Delta T = \frac{p}{R}\Delta V \qquad (2.11)$$

i.e. the temperature increase is proportional to the observed volume increase. The constant volume gas thermometer is, however, mostly in use, since it is simpler in construction and easier to operate.

2.6 IDEAL GAS TEMPERATURE

Let us suppose that the bulb of a constant volume gas thermometer contains an amount of gas such that when the bulb is surrounded by water at its triple point, the pressure p_t is 1000 mmHg. Keeping the volume V constant, let the following procedure be conducted:

(a) Surround the bulb with steam condensing at 1 atm, determine the gas pressure p and calculate

$$\theta = 273.16 \, \frac{p}{1000}$$

(b) Remove some gas from the bulb so that when it is surrounded by water at its triple point, the pressure p_t is 500 mmHg. Determine the new value of p and then θ for steam condensing at 1 atm.

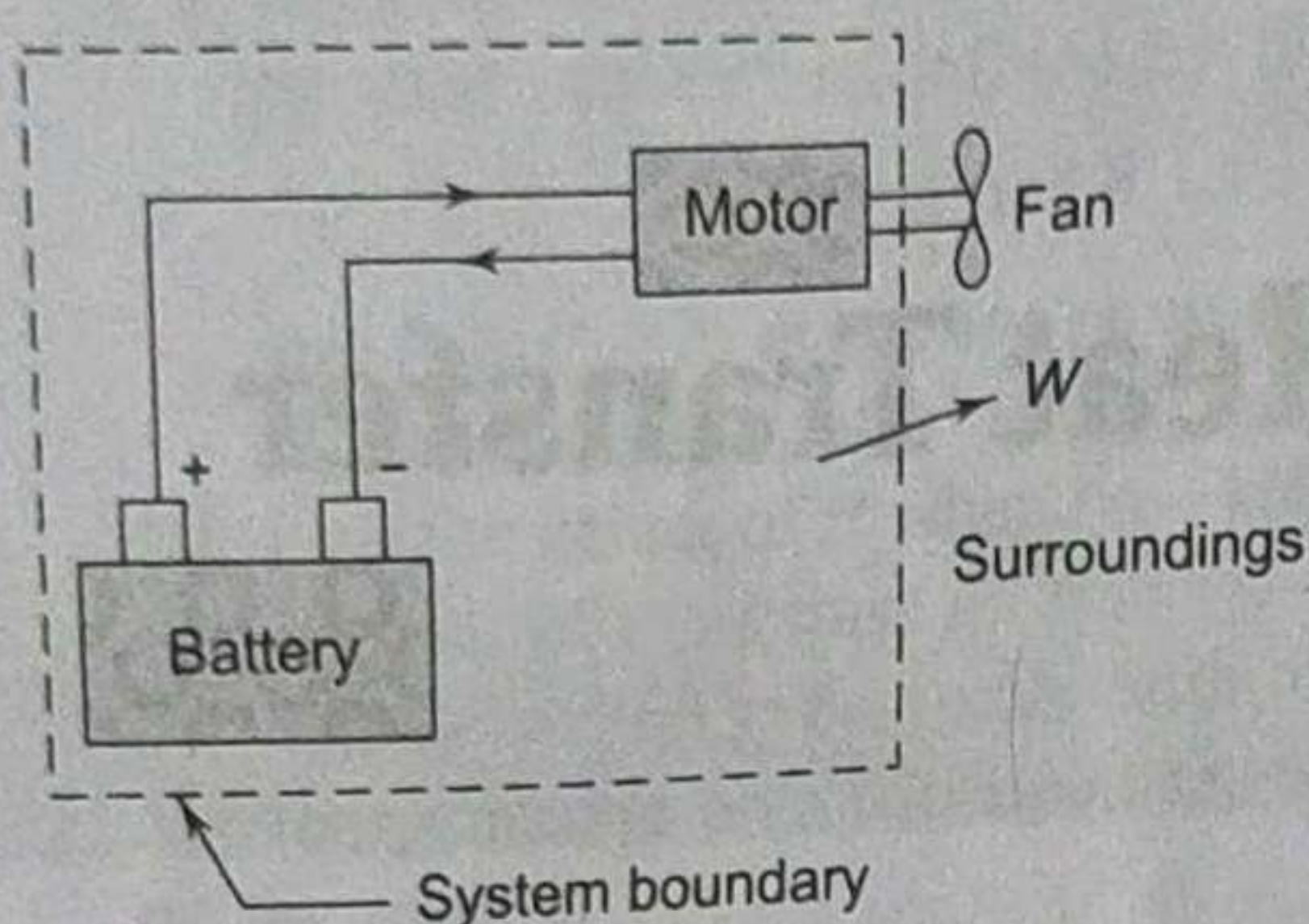$$\theta = 273.16 \, \frac{p}{500}$$
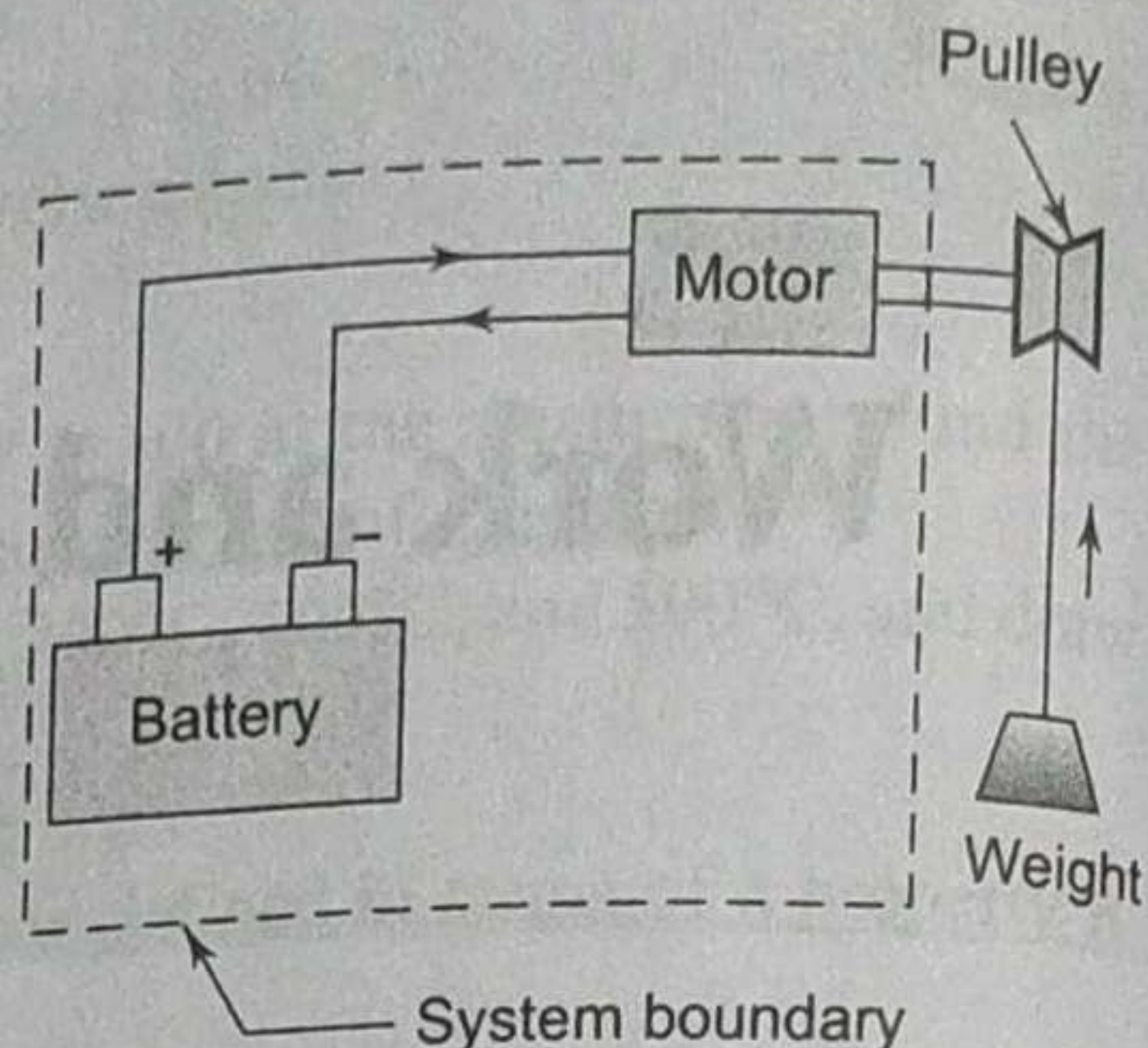
Fig. 3.1   *Battery-motor System Driving a Fan*

Fig. 3.2   *Work Transfer from a System*

When work is done by a system, it is arbitrarily taken to be positive, and when work is done on a system, it is taken to be negative (Fig. 3.3). The symbol W is used for work transfer.
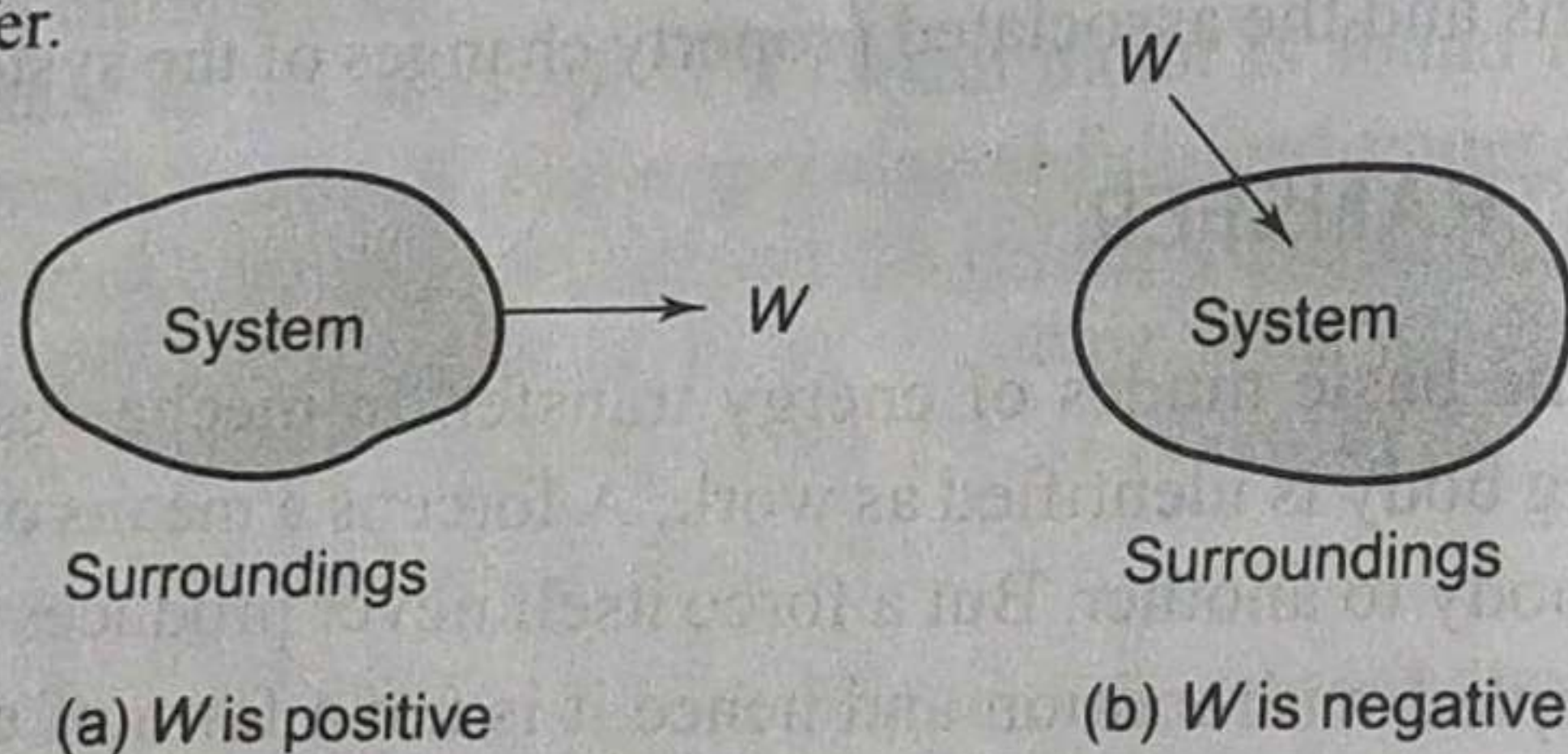

(a) W is positive

(b) W is negative

Fig. 3.3 *Work Interaction between a System and the Surroundings*

The unit of work is N.m or Joule [1 Nm = 1 Joule]. The rate at which work is done by, or upon, the system is known as *power*. The unit of power is J/s or watt.

Work is one of the forms in which a system and its surroundings can interact with each other. There are various types of work transfers which can get involved between them.

3.2   pdV-WORK OR DISPLACEMENT WORK

Let the gas in the cylinder (Fig. 3.4) be a system having initially the pressure p_1 and volume V_1. The system is in thermodynamic equilibrium, the state of which is described by the coordinates p_1, V_1. The piston is the only boundary which moves due to gas pressure. Let the piston move out to a new final position 2, which is also a thermodynamic equilibrium state specified by pressure p_2 and volume V_2. At any intermediate point in the travel of the piston, let the pressure be p and the volume V. This must also be an equilibrium state, since macroscopic properties p and V are
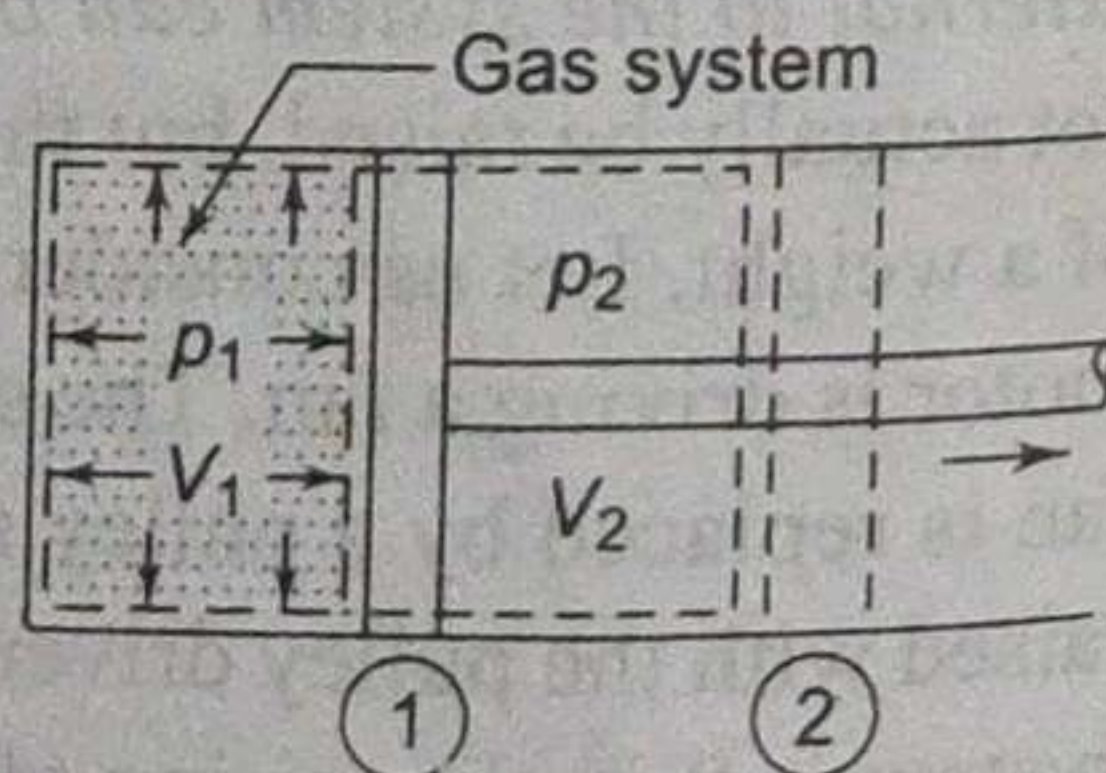

Fig. 3.4   *pdV Work*

significant only for equilibrium states. When the piston moves an infinitesimal distance dl, and if 'a' be the area of the piston, the force F acting on the piston $F = p.a$. and the infinitesimal amount of work done by the gas on the piston

$$dW = F \cdot dl = padl = pdV \qquad (3.1)$$

where $dV = adl$ = infinitesimal displacement volume. The differential sign in dW with the line drawn at the top of it will be explained later.

When the piston moves out from position 1 to position 2 with the volume changing from V_1 to V_2, the amount of work W done by the system will be

$$W_{1-2} = \int_{V_1}^{V_2} pdV$$

The magnitude of the work done is given by the area under the path 1–2, as shown in Fig. 3.5. Since p is at all times a thermodynamic coordinate, all the states passed through by the system as the volume changes from V_1 to V_2 must be equilibrium states, and the path 1–2 *must be quasi-static*. The piston moves infinitely slowly so that every state passed through is an equilibrium state. The integration $\int pdV$ can be performed only on a quasi-static path.
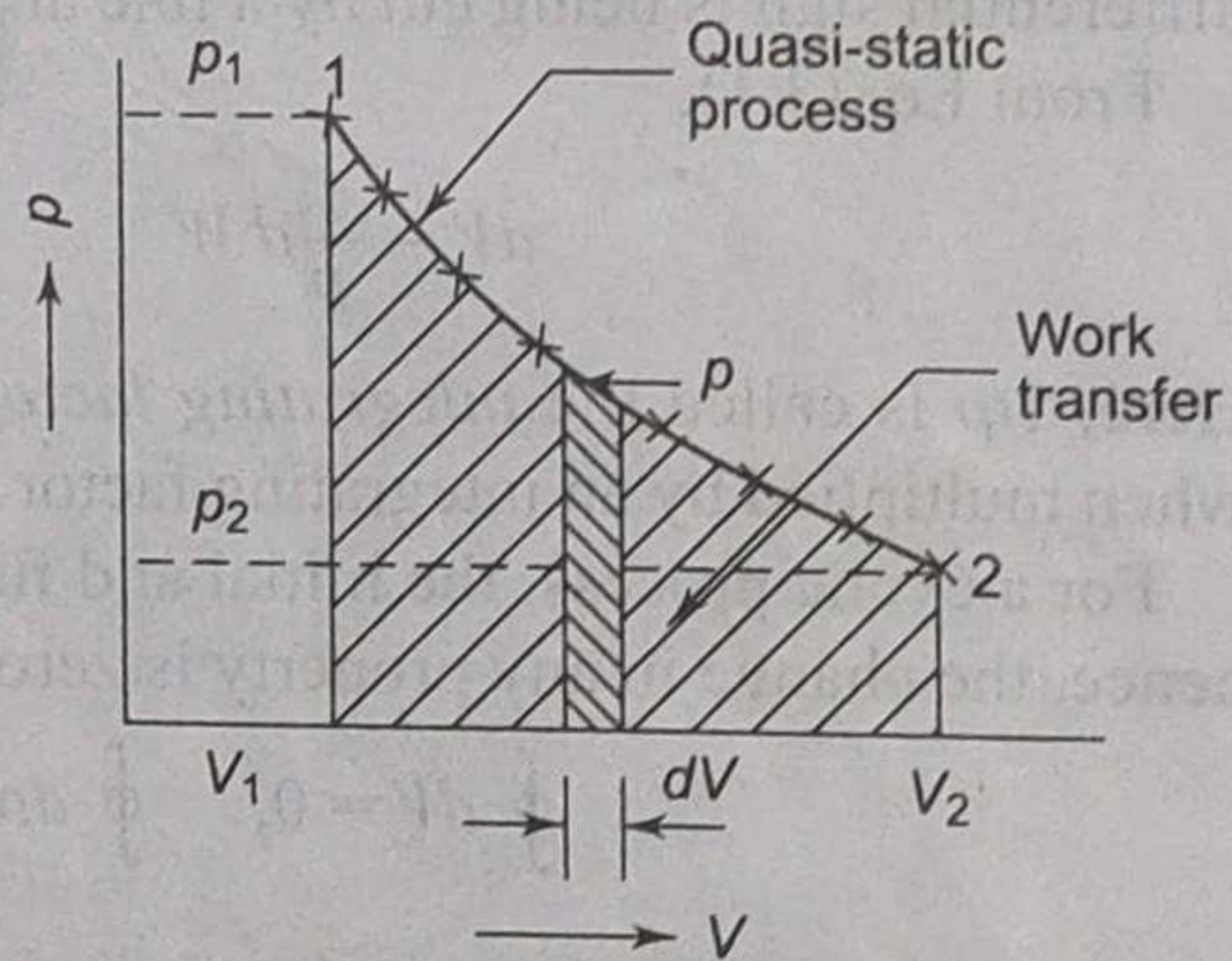

Fig. 3.5   *Quasi-Static pdV Work*

3.2.1   Path Function and Point Function

With reference to Fig. 3.6, it is possible to take a system from state 1 to state 2 along many quasi-static paths, such as A, B or C. Since the area under each curve represents the work for each process, the amount of work involved in each case is not a function of the end states of the process, and it depends on the path the system follows in going from state 1 to state 2. For this reason, work is called a *path function*, and dW is an *inexact or imperfect differential*.

Thermodynamic properties are *point functions*, since for a given state, there is a definite value for each property. The change in a thermodynamic property of a system in a change of state is independent of the path the system follows during the change of state, and depends only on the initial and final states of the system. The differentials of point functions are *exact or perfect differentials*, and the integration is simply.
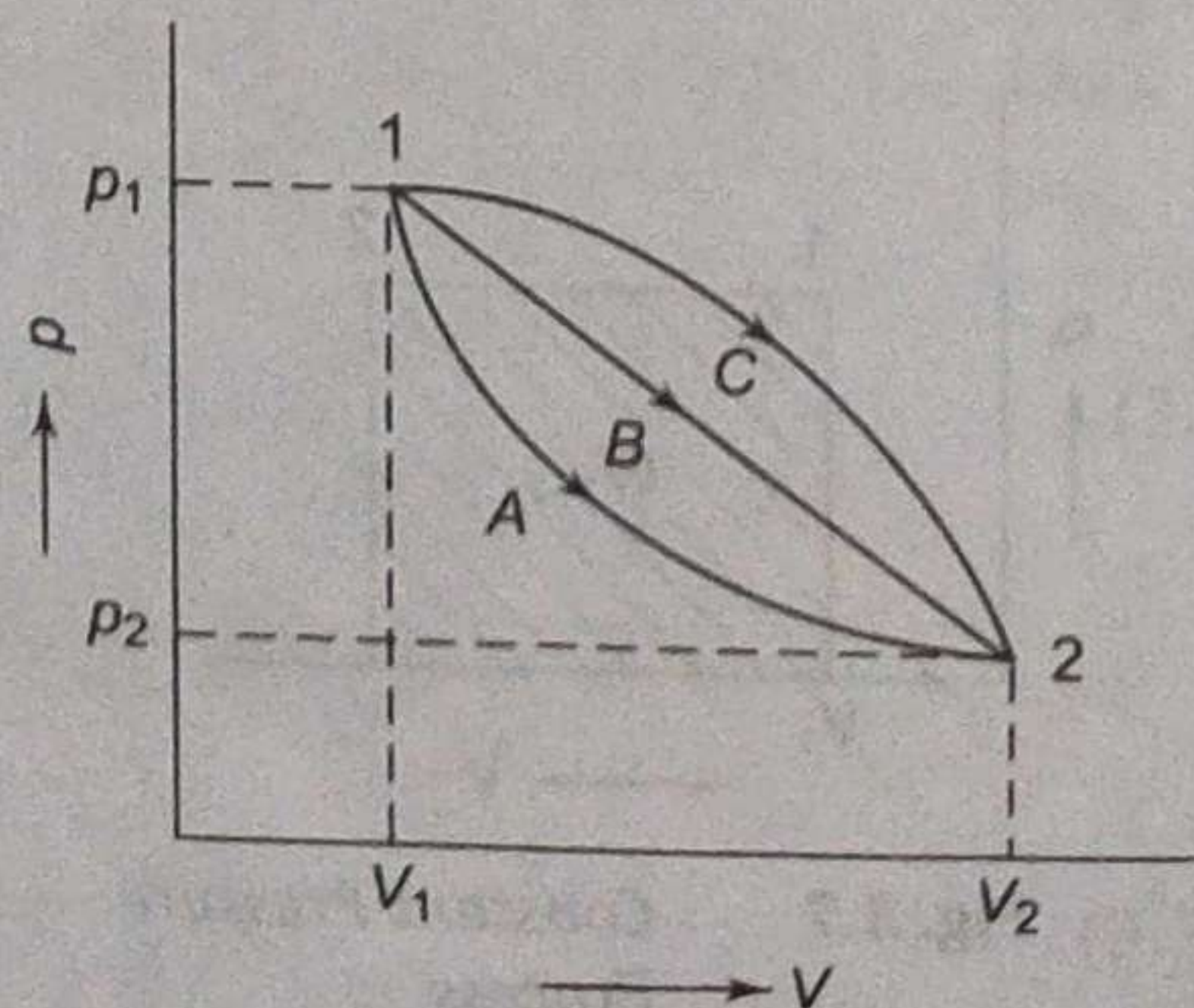
$$\int_{V_1}^{V_2} dV = V_2 - V_1$$

Fig. 3.6   *Work—A Path Function*

6.4 KELVIN-PLANCK STATEMENT OF SECOND LAW

The efficiency of a heat engine is given by

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

Experience shows that $W_{net} < Q_1$, since heat Q_1 transferred to a system cannot be completely converted to work in a cycle (Article 6.1). Therefore, η is less than unity. A heat engine can never be 100% efficient. Therefore, $Q_2 > 0$, i.e. there has always to be a heat rejection. To produce net work in a thermodynamic cycle, a heat engine has thus to exchange heat with two reservoirs, the source and the sink.

The *Kelvin-Planck statement* of the second law states: *It is impossible for a heat engine to produce net work in a complete cycle if it exchanges heat only with bodies at a single fixed temperature.*

If $Q_2 = 0$ (i.e. $W_{net} = Q_1$, or $\eta = 1.00$), the heat engine will produce net work in a complete cycle by exchanging heat with only one reservoir, thus violating the Kelvin-Planck statement (Fig. 6.5). Such a heat engine is called a *perpetual motion machine of the second kind*, abbreviated to PMM2. A PMM2 is impossible.

A heat engine has, therefore, to exchange heat with two thermal energy reservoirs at two different temperatures to produce net work in a complete cycle (Fig. 6.6). So long as there is a difference in temperature, motive power (i.e. work) can be produced. If the bodies with which the heat engine exchanges heat are of finite heat capacities, work will be produced by the heat engine till the temperatures of the two bodies are equalized.
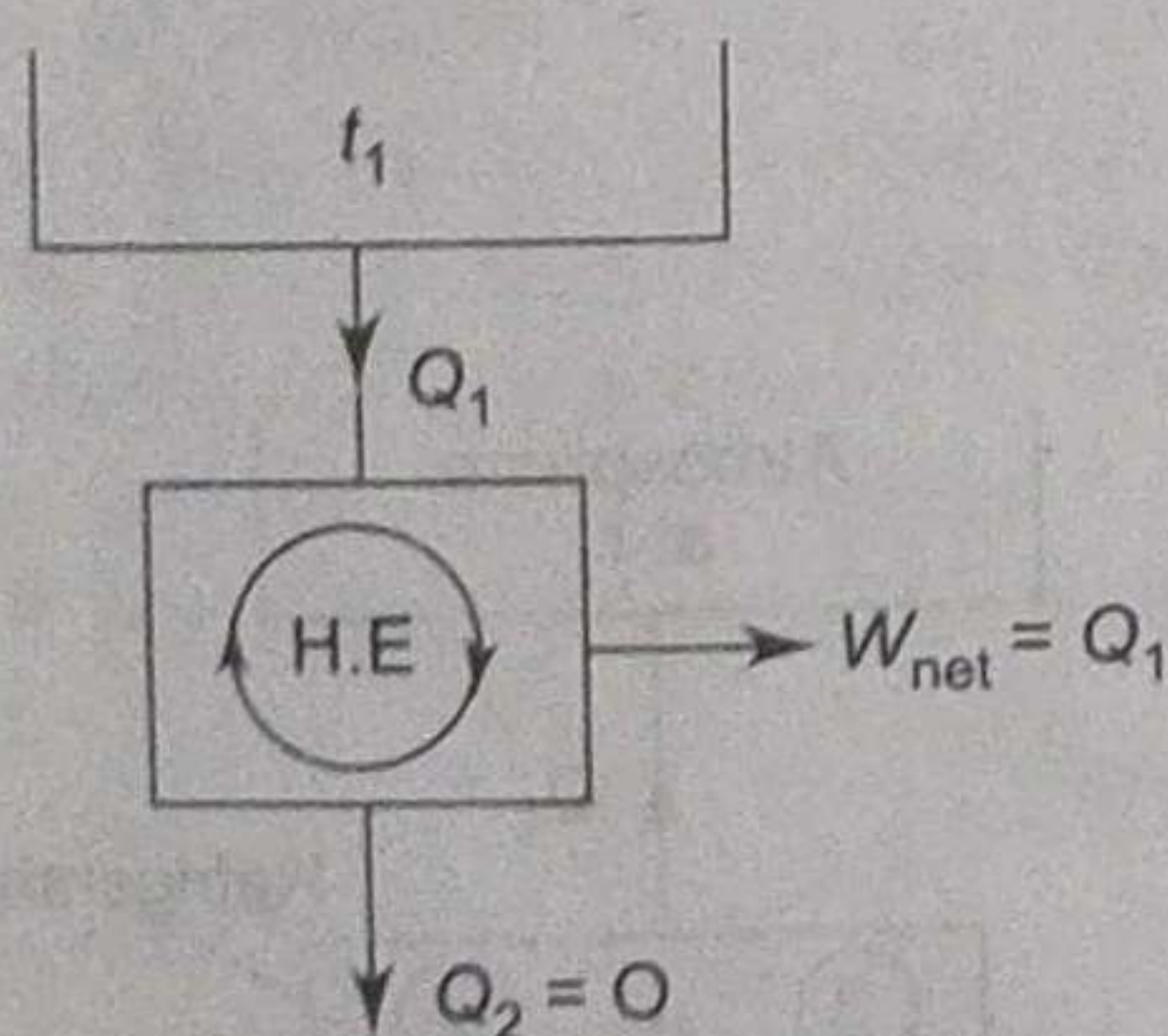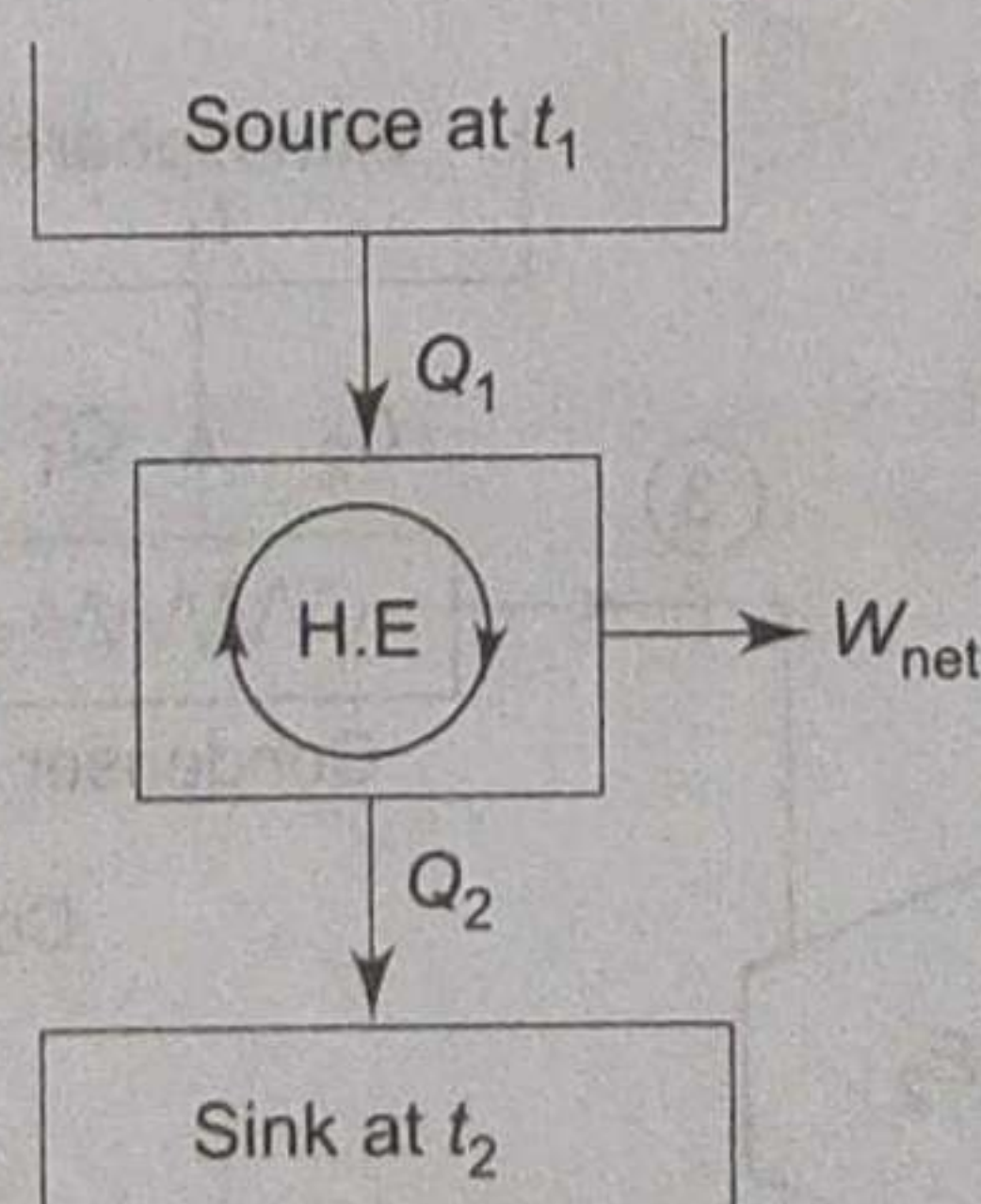

Fig. 6.5 A PMM2

Fig. 6.6 *Heat Engine Producing Net Work in a Cycle by Exchanging Heat at Two Different Temperatures*

6.5 CLAUSIUS' STATEMENT OF THE SECOND LAW

Heat always flows from a body at a higher temperature to a body at a lower temperature. The reverse process never occurs spontaneously.

Clausius' statement of the second law gives: *It is impossible to construct a device which, operating in a cycle, will produce no effect other than the transfer of heat from a cooler to a hotter body.*

Heat cannot flow of itself from a body at a lower temperature to a body at a higher temperature. Some work must be expended to achieve this.

6.6 REFRIGERATOR AND HEAT PUMP

A *refrigerator* is a device which, operating in a cycle, maintains a body at a temperature lower than the temperature of the surroundings. Let the body A (Fig. 6.7) be maintained at t_2, which is lower than the ambient temperature t_1. Even though A is insulated, there will always be heat leakage Q_2 into the body from the surroundings by virtue of the temperature difference. In order to maintain body A at the constant temperature t_2, heat has to be removed from the body at the same rate at which heat is leaking into the body. This heat (Q_2) is absorbed by a working fluid, called the refrigerant, which evaporates in the evaporator E_1 at a temperature lower than t_2 absorbing the latent heat of vaporization from the body A which is cooled or refrigerated (Process 4–1). The vapour is first compressed in the compressor C_1 driven by a motor which absorbs work W_C (Process 1–2), and is then condensed in the condenser C_2 rejecting the latent heat of condensation Q_1 at a temperature higher than that of the atmosphere (at t_1) for heat transfer to take place (Process 2–3). The condensate then expands adiabatically through an expander (an engine or turbine) producing work W_E, when the temperature drops to a value lower than t_2 such that heat Q_2 flows from the body A to make the refrigerant evaporate (Process 3–4). Such a cyclic device of flow through E_1–C_1–C_2–E_2 is called a *refrigerator*. In a
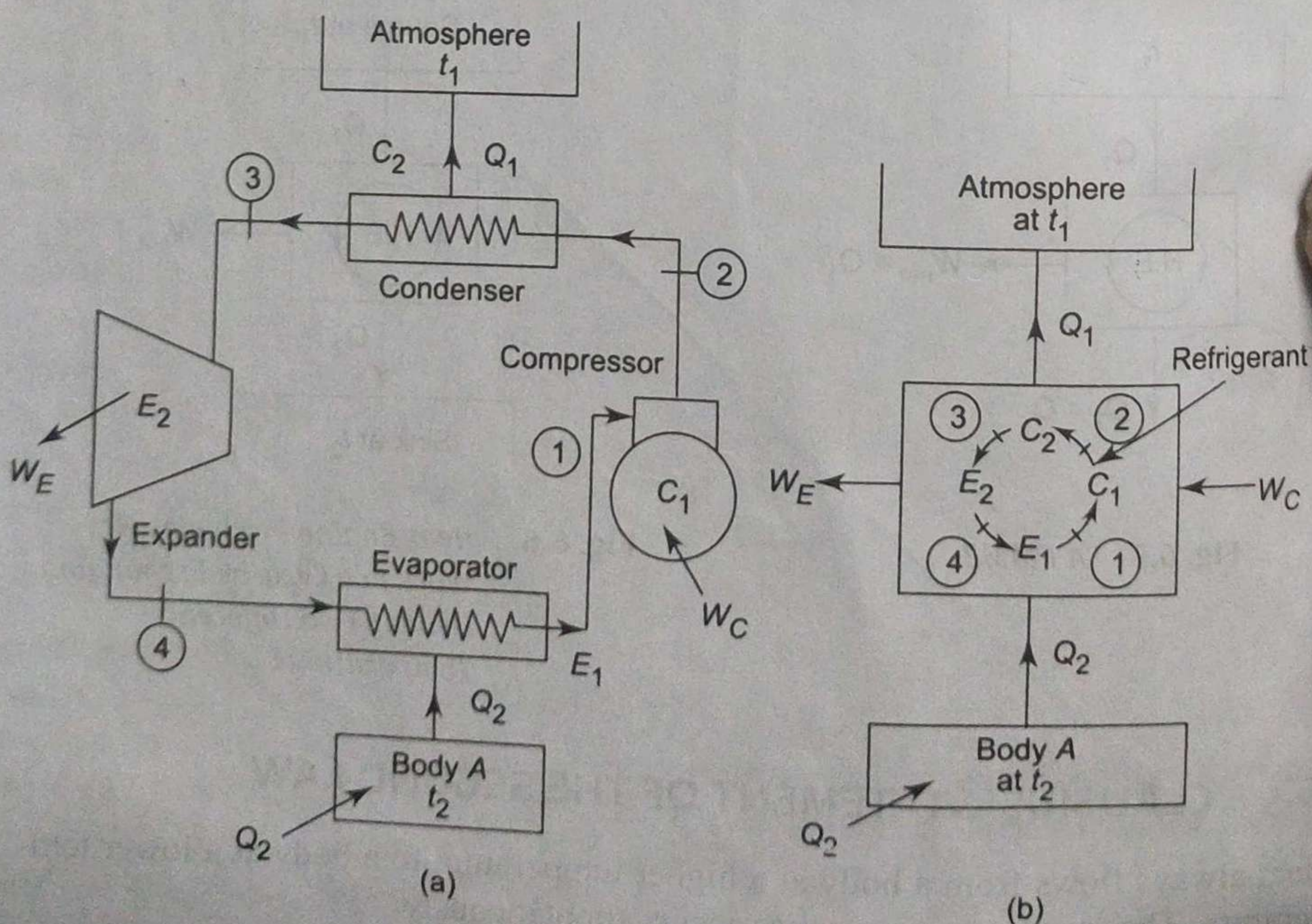

Fig. 6.7   *A Cyclic Refrigeration Plant*