ENGINEERING THERMODYNAMICS

BME-12(III Sem. ME)

by

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Fundamental Concepts and Definitions

Introduction and definition of thermodynamics, Microscopic and Macroscopic approaches, Concept of continuum .Systems, surroundings, Control system, control volume and control surface, Properties, intensive & extensive and state of Thermodynamic system. point and path properties, process, cycle , Thermodynamic equilibrium, Reversibility and irreversibility, Quasi static process, Energy and its forms, Work and heat, Ideal & Real gas, Dalton’s law, Amagat’s law, Property of mixture of gases.

Zeroth law of thermodynamics

Zeroth law of thermodynamics, Temperature and its’ measurement.

First law of thermodynamics for closed system

Introduction of first law of thermodynamics, Calculation of work in various processes and sign convention, work, Joules’ experiment, Internal energy and enthalpy

DEFINITION OF THERMODYNAMICS

- *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 that deals with the interaction between energy and material systems.*

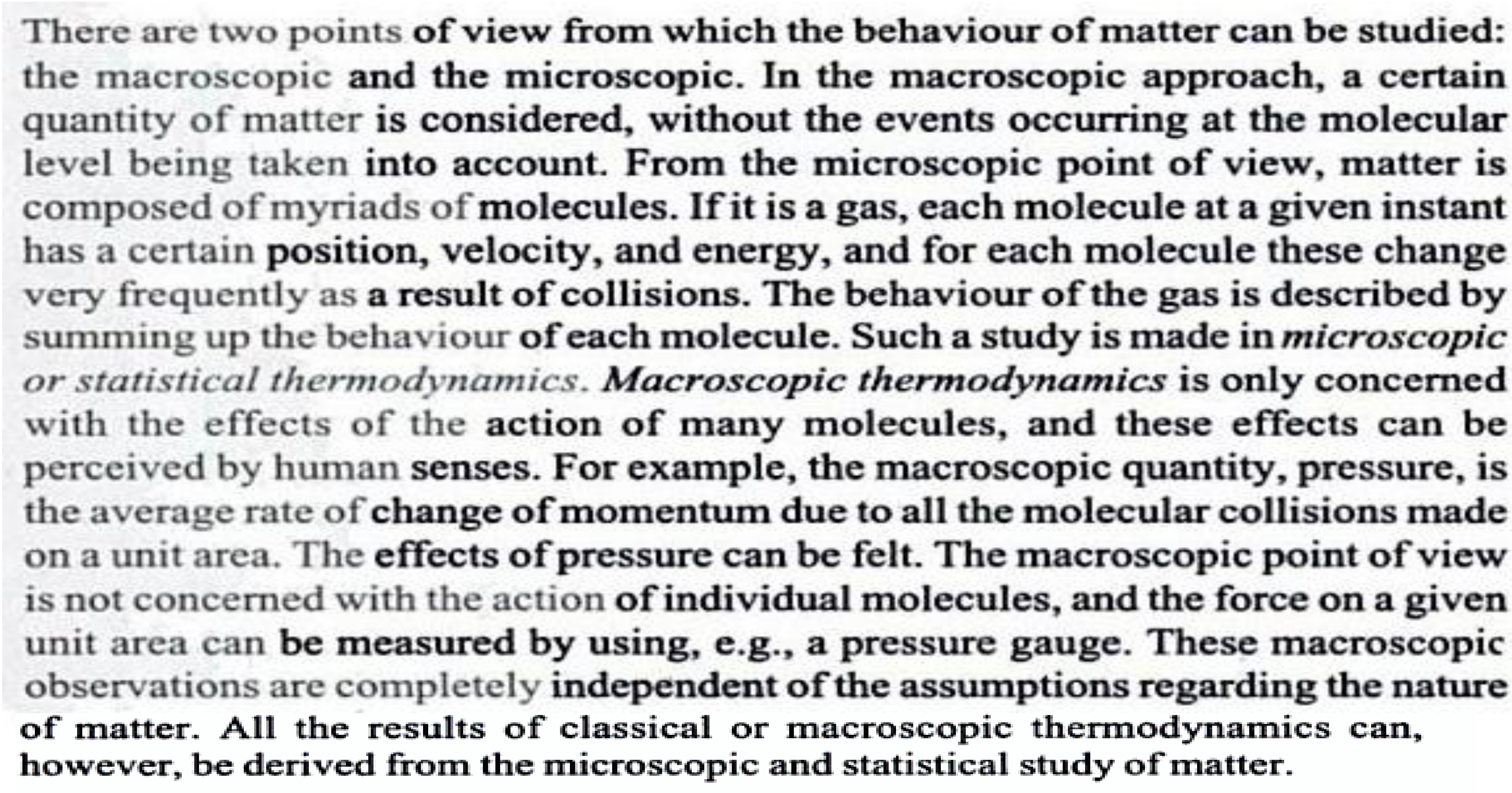
- ‘’Thermodynamics is the branch of physical science that deals with the various phenomena of energy and related properties of matter, especially of the laws of transformations of heat into other forms of energy and vice-versa.”

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.*
- The ***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.*

Macroscopic Vs Microscopic Viewpoint



There are two points of view from which the behaviour of matter can be studied: the macroscopic and the microscopic. In the macroscopic approach, a certain quantity of matter is considered, without the events occurring at the molecular level being taken into account. From the microscopic point of view, matter is composed of myriads of molecules. If it is a gas, each molecule at a given instant has a certain position, velocity, and energy, and for each molecule these change very frequently as a result of collisions. The behaviour of the gas is described by summing up the behaviour of each molecule. Such a study is made in *microscopic or statistical thermodynamics*. *Macroscopic thermodynamics* is only concerned with the effects of the action of many molecules, and these effects can be perceived by human senses. For example, the macroscopic quantity, pressure, is the average rate of change of momentum due to all the molecular collisions made on a unit area. The effects of pressure can be felt. The macroscopic point of view is not concerned with the action of individual molecules, and the force on a given unit area can be measured by using, e.g., a pressure gauge. These macroscopic observations are completely independent of the assumptions regarding the nature of matter. All the results of classical or macroscopic thermodynamics can, however, be derived from the microscopic and statistical study of matter.

Concept of Continuum

In Macroscopic approach of thermodynamics the substance is considered to be continuous whereas every matter actually comprises of myriads of molecules with intermolecular spacing amongst them. For analyzing a substance in aggregate it shall be desired to use laws of motion for individual molecules and study at molecular level be put together statistically to get the influence upon aggregate. In statistical thermodynamics this microscopic approach is followed, although it is often too cumbersome for practical calculations.

In engineering thermodynamics where focus lies upon the gross behaviour of the system and substance in it, the statistical approach is to be kept aside and classical thermodynamics approach be followed. In classical thermodynamics, for analysis the atomic structure of substance is considered to be continuous. For facilitating the analysis this concept of continuum is used in which the substance is treated free from any kind of discontinuity. As this is an assumed state of continuum in substance so the order of analysis or scale of analysis becomes very important. Thus, in case the scale of analysis is large enough and the discontinuities are of the order of intermolecular spacing or mean free path then due to relative order of discontinuity being negligible it may be treated continuous.

Thermodynamic systems, Boundary and Surroundings

System

A system is *a finite quantity of matter or a prescribed region of space.*

Boundary

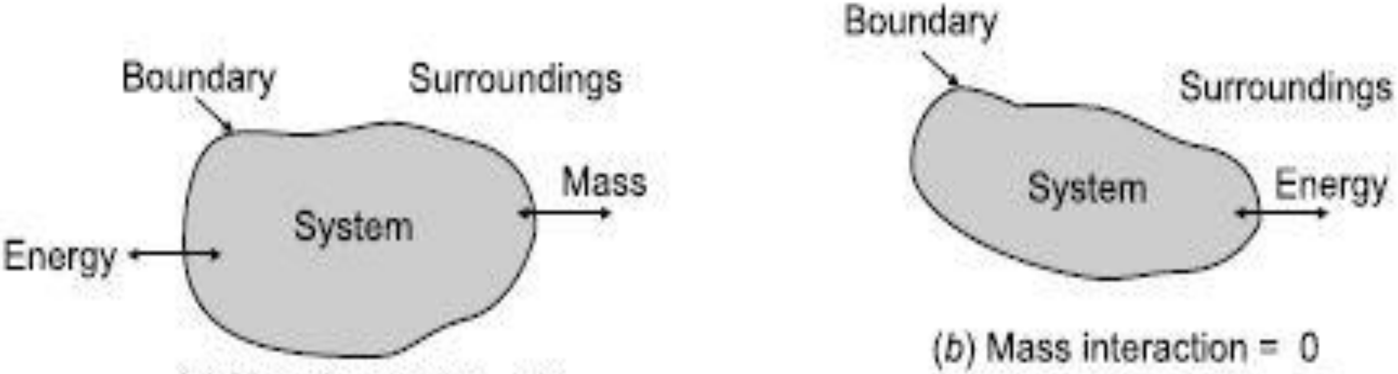
The *actual or hypothetical envelope enclosing the system is the boundary of the* system. The boundary may be fixed or it may move. The boundary may be *real or imaginary.*

- In thermodynamics the ‘system’ is defined as the quantity of matter or region in space upon which the attention is concentrated for the sake of analysis. These systems are also referred to as thermodynamic systems. For the study these systems are to be clearly defined using a real or hypothetical boundary.

- Every thing outside this real/hypothetical boundary is termed as the ‘surroundings’. Thus, the surroundings may be defined as every thing surrounding the system.
- System and surroundings when put together result in universe.

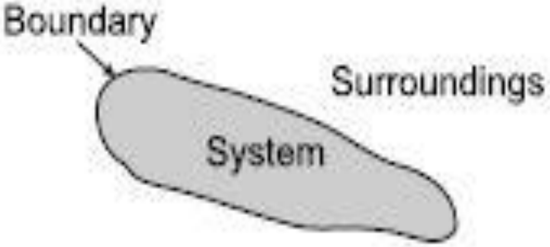
  Universe = System + Surroundings
- The system is also some times defined as the control system and the boundary defined for separating it from surroundings is called control boundary, the volume enclosed within the boundary is control volume and the space enclosed within the boundary is called control space.

- Based on the energy and mass interactions of the systems with the surrounding can be further classified as the open, close, and isolated system.
- The open system is one in which the energy and mass interactions take place at the system boundary, for example automobile engine etc.
- Closed system is the system having only energy interactions at its boundary, for example, boiling water in a closed pan etc. The mass interactions in such system are absent.
- Isolated system refers to the system which neither has mass interaction nor energy interaction across system boundary for example Thermos Flask etc. Thus, the isolated system does not interact with the surroundings/systems in any way.



(*a*) Mass interaction ≠ 0
Energy interaction ≠ 0

(*b*) Mass interaction = 0
Energy interaction ≠ 0



(*c*) Mass interaction = 0
Energy interaction = 0

Figure-1(a) Open system (b) Closed system (c) Isolated system

Homogeneous and Heterogeneous Systems

A quantity of matter homogeneous throughout in chemical composition and physical structure is called a *phase*. Every substance can exist in any one of the three phases, viz., solid, liquid and gas. A system consisting of a single phase is called a *homogeneous system*, while a system consisting of more than one phase is known as a *heterogeneous system.*

Homogeneous and Heterogeneous system

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.

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.

Open, closed, adiabatic system

- **Closed System** :- *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.

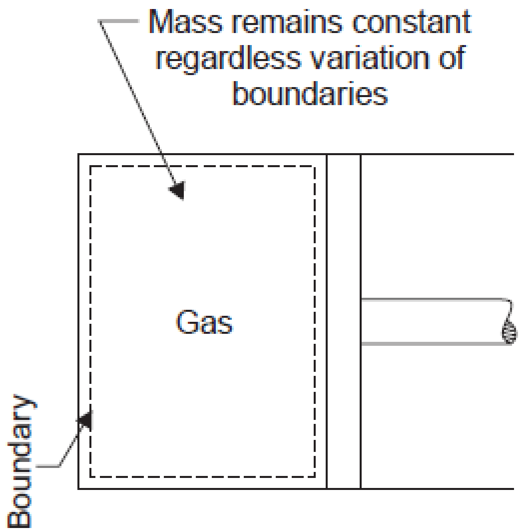


Figure-2 :Closed system

Example of open System

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

Examples :- Turbines, pumps and nozzles etc.

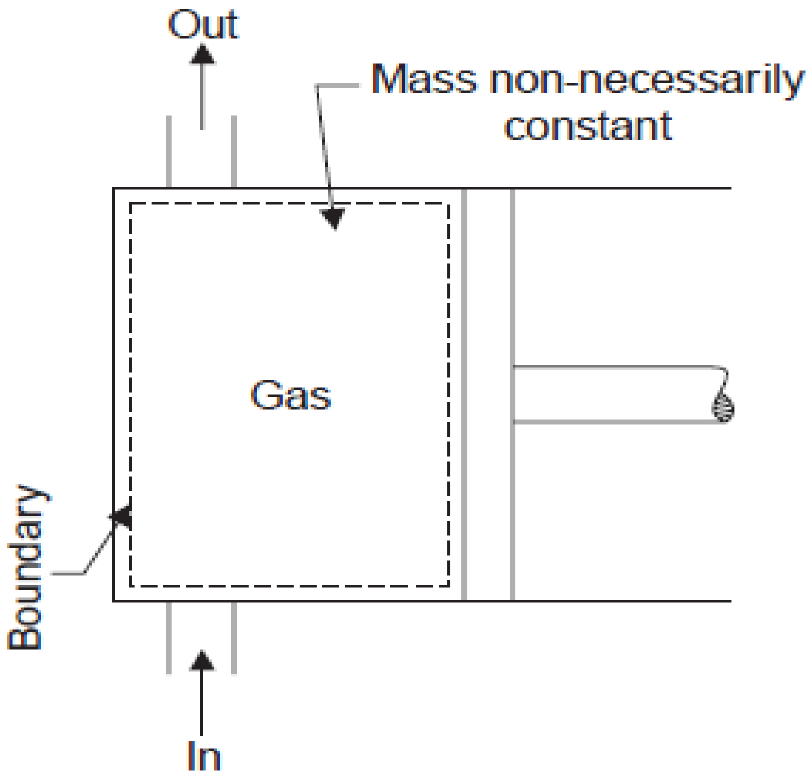


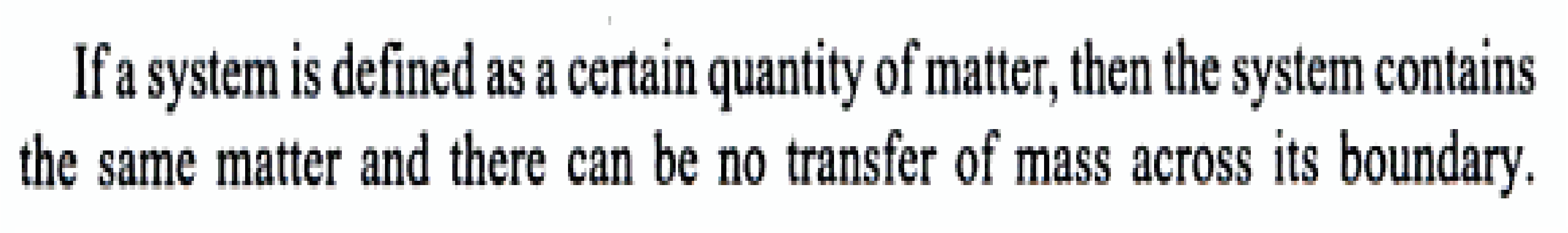
Figure-3 : Open system

Isolated and adiabatic system

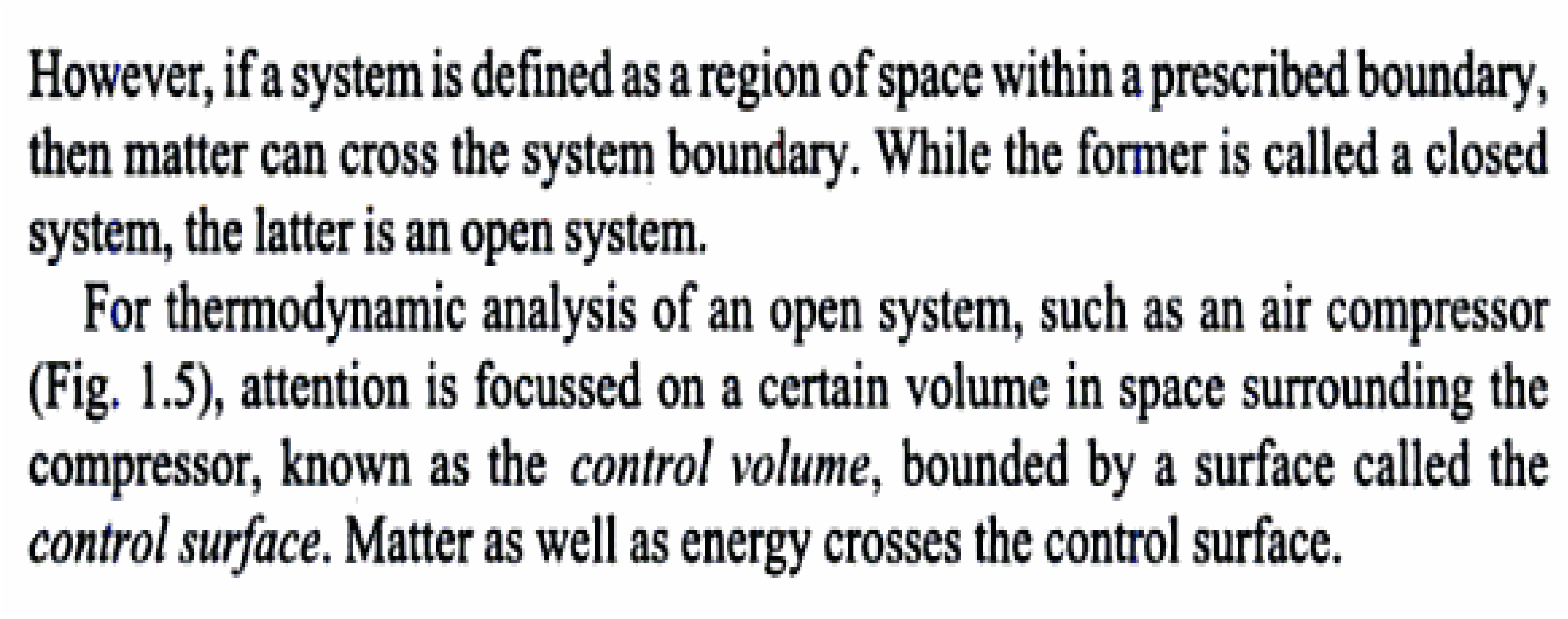
- Isolated System
- An isolated system is that system *which exchanges neither energy nor matter with any*
- *other system or with environment.*

- 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.*

Control volume and control surface



If a system is defined as a certain quantity of matter, then the system contains the same matter and there can be no transfer of mass across its boundary.



However, if a system is defined as a region of space within a prescribed boundary, then matter can cross the system boundary. While the former is called a closed system, the latter is an open system.

For thermodynamic analysis of an open system, such as an air compressor (Fig. 1.5), attention is focussed on a certain volume in space surrounding the compressor, known as the *control volume*, bounded by a surface called the *control surface*. Matter as well as energy crosses the control surface.

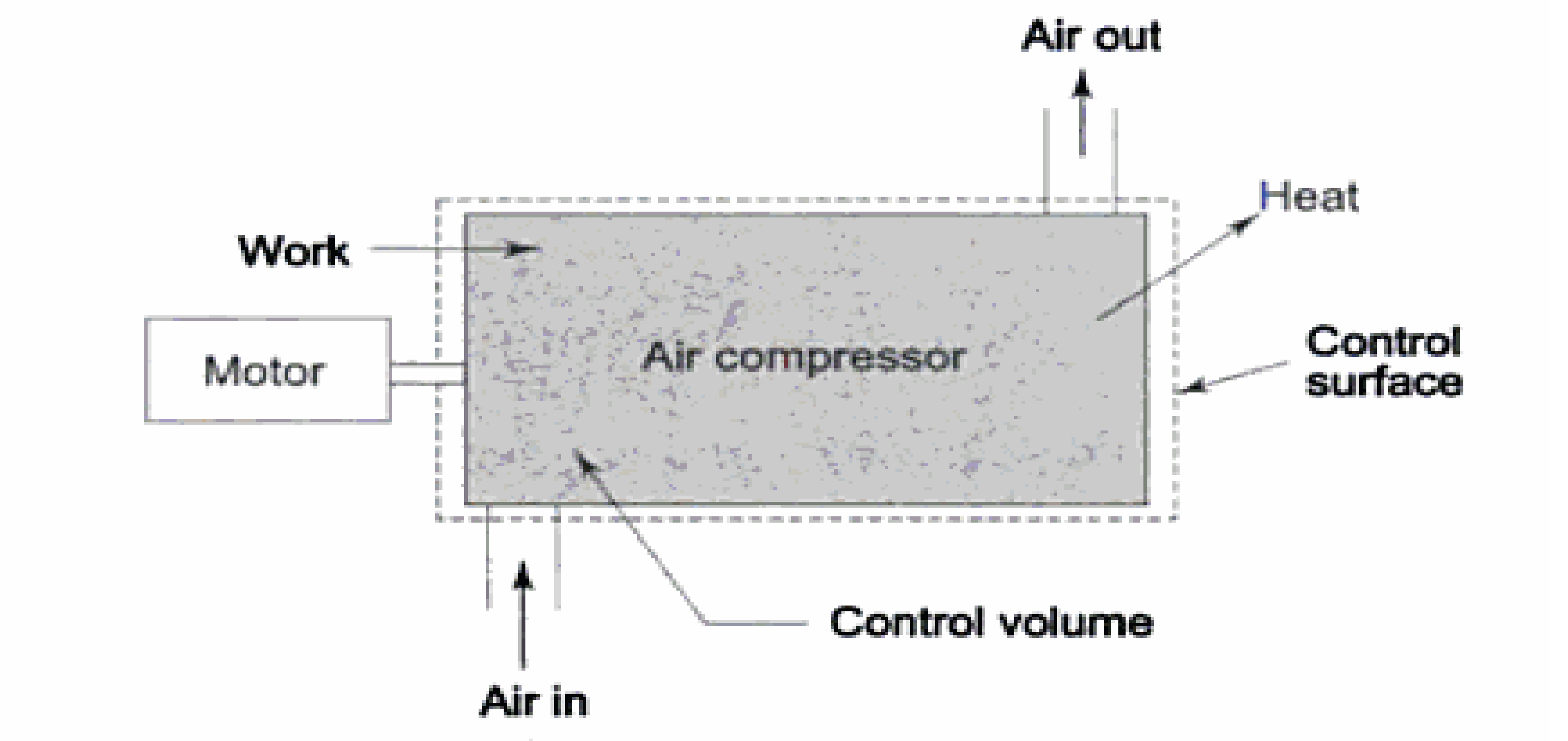
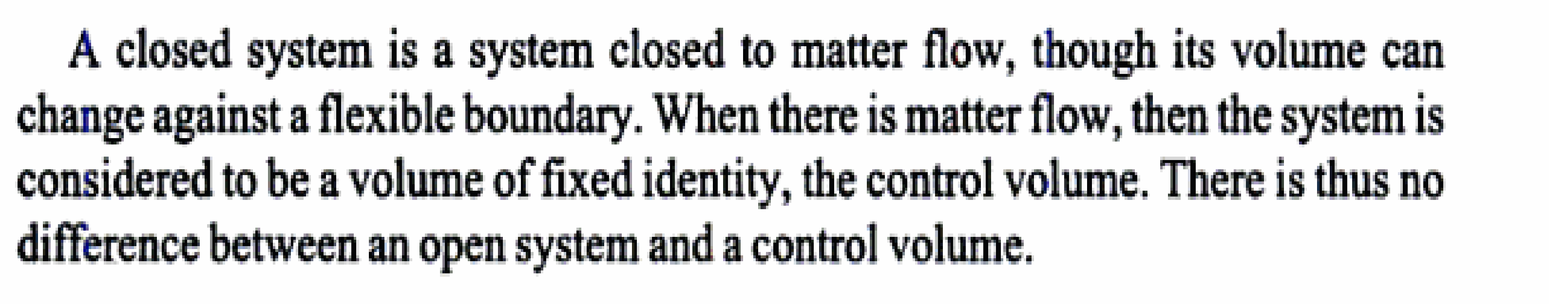


Fig. Control volume and control surface



A closed system is a system closed to matter flow, though its volume can change against a flexible boundary. When there is matter flow, then the system is considered to be a volume of fixed identity, the control volume. There is thus no difference between an open system and a control volume.

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.

THERMODYNAMIC EQUILIBRIUM

- A system is in state of thermodynamic equilibrium if it has the following :

  (1)The temperature and pressure at all points are same

  (2) There should be no velocity gradient and chemical reaction within a system.

  (3) The chemical equilibrium is also necessary.

  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.

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 types 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 , enthalpy and entropy

  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 $V/m = v$ which is an intensive property.

State and Property

- 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.
- 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 :

(1) A variable is a property only if, it has a single value at each equilibrium state.

(2) 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.

Path , Process and cycle

- A path is a locus of different states passed by the system. When this path is specified is known as process.
- A thermodynamic cycle is a combination of different processes , which a system follows and finally comes to initial state.

- Process on a p-v diagram

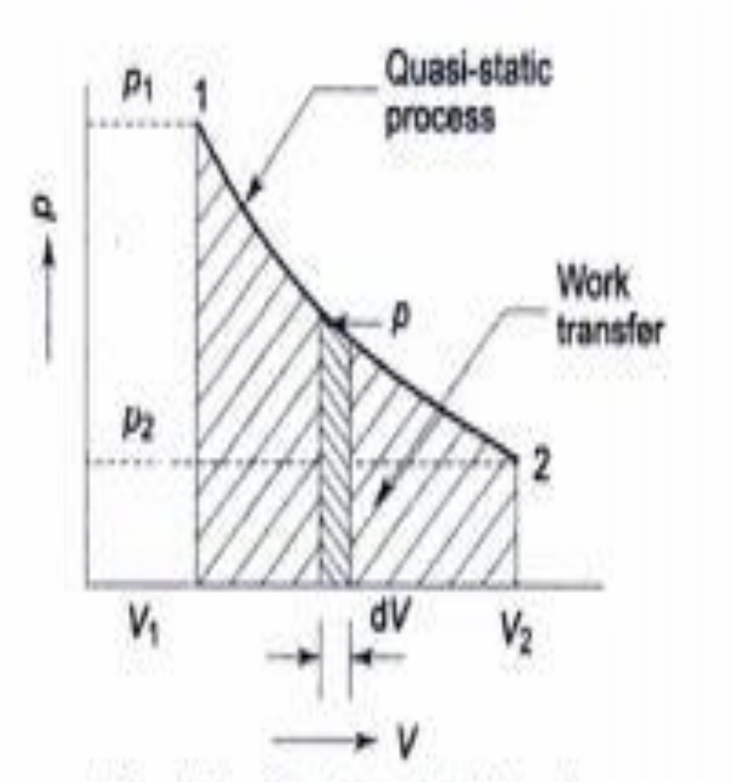
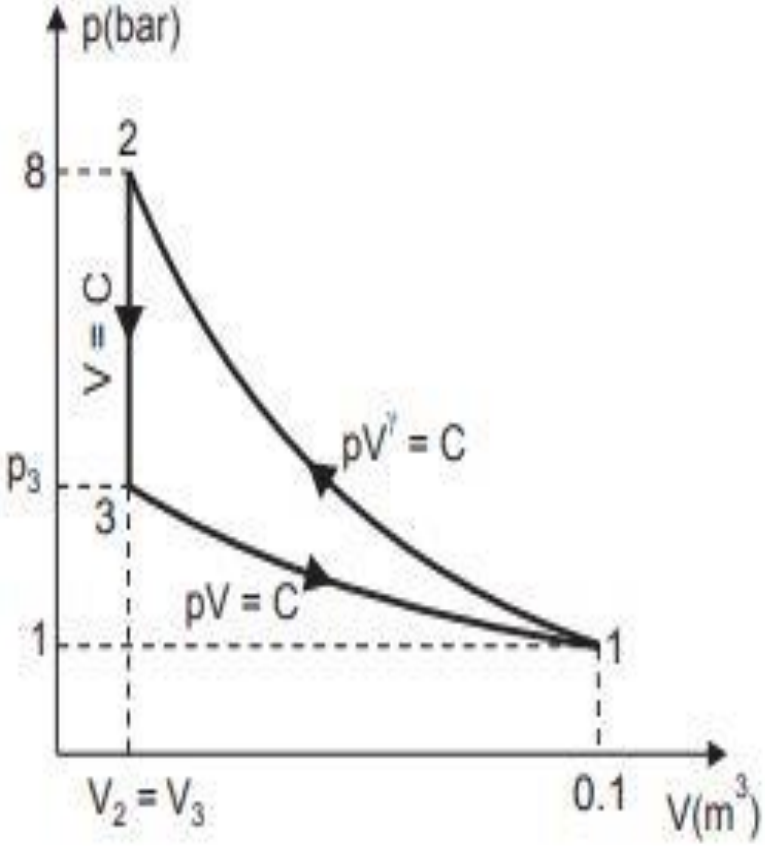


Fig. 3.5 *Quasi-static pdV work*

- Cycle on a p-v diagram



Quasi-static process

- **Quasi-static process:** A quasi-static process is an infinitely slow process and also called a reversible process. This process is a succession of equilibrium states and infinite slowness is its characteristic feature.
- Quasistatic process passes through different equilibrium points between the starting and end states of a reversible process.

- Let us consider the heating of gas in a container with certain mass ‘W’ kept on the top of lid (lid is such that it does not permit leakage across its interface with vessel wall) of the vessel as shown in Fig. After certain amount of heat being added to the gas it is found that the lid gets raised up. Thermodynamic state change is shown in Fig. The “change in state” is significant. During the change of state since the states could not be considered to be in equilibrium, hence for unsteady state of system thermodynamic analysis could not be extended.

Let us now assume that the total mass comprises of infinitesimal small masses of ‘*w’ such that all ‘w’ masses put together become equal to W. Now let us* start heat addition to vessel and as soon as the lifting of lid is observed put first fraction mass ‘*w’ over* the lid so as to counter the lifting and estimate the state change. During this process it is found that the state change is negligible. Let us further add heat to the vessel and again put the second fraction mass‘*w’ as soon as the lift is felt so as to counter it. Again the state change is seen to be negligible. Continue* with the above process and at the end it shall be seen that all fraction masses ‘*w’ have been put over the* **lid**, thus amounting to mass ‘*W’ kept over the lid of vessel and the state change occurred is exactly similar to the* one which occurred when the mass kept over the lid was ‘*W’. In this way the equilibrium nature of* system can be maintained and the thermodynamic analysis can be carried out. *p-v representation for the* series of infinitesimal state changes occurring between states 1 and 2 is shown in Fig. 1.4.

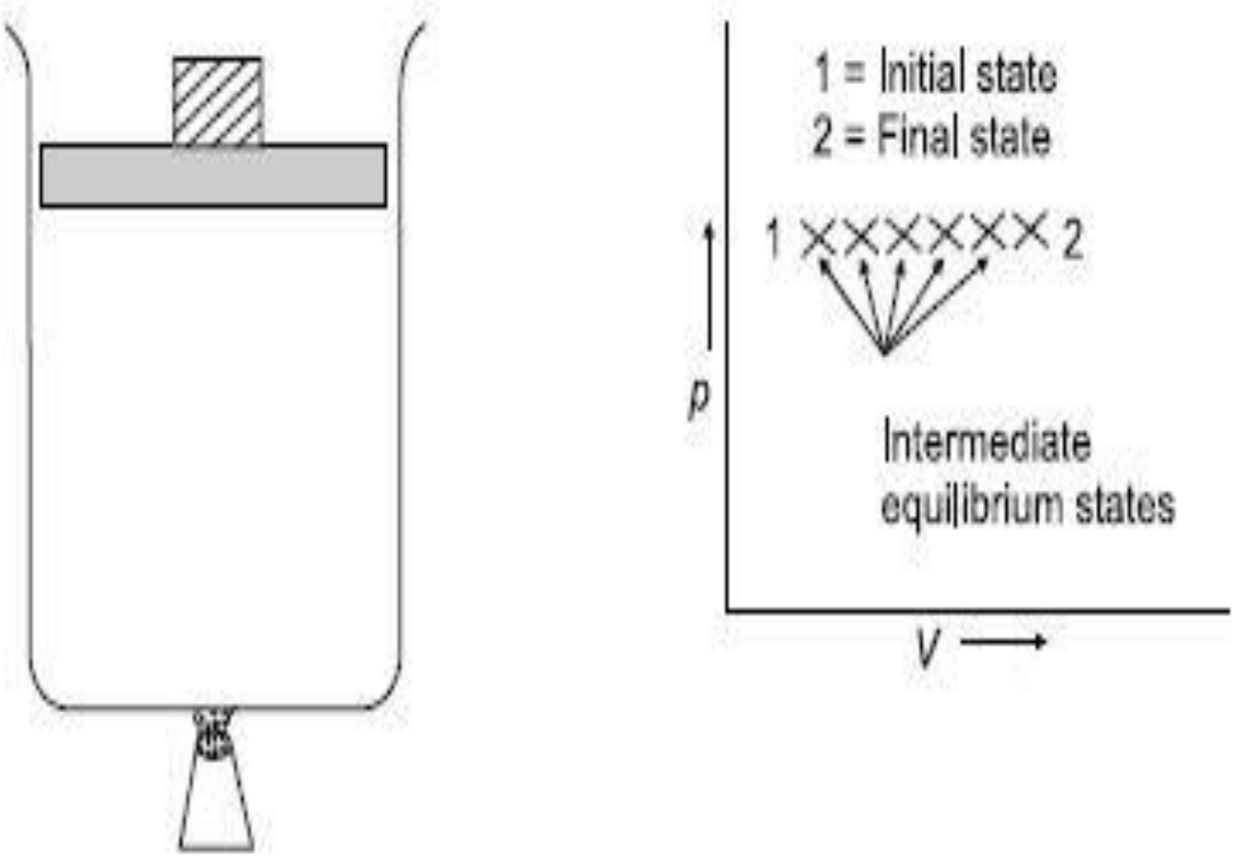


Figure-5 :- Quasistatic Process

Reversible and Irreversible processes

2.18. 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.

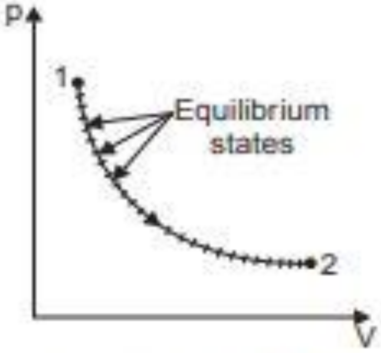


Fig. 2.29. Reversible process.

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

Examples. Some examples of nearly reversible processes are :

(*i*) Frictionless relative motion.

(*ii*) Expansion and compression of spring.

(*iii*) Frictionless adiabatic expansion or compression of fluid.

(*iv*) Polytropic expansion or compression of fluid.

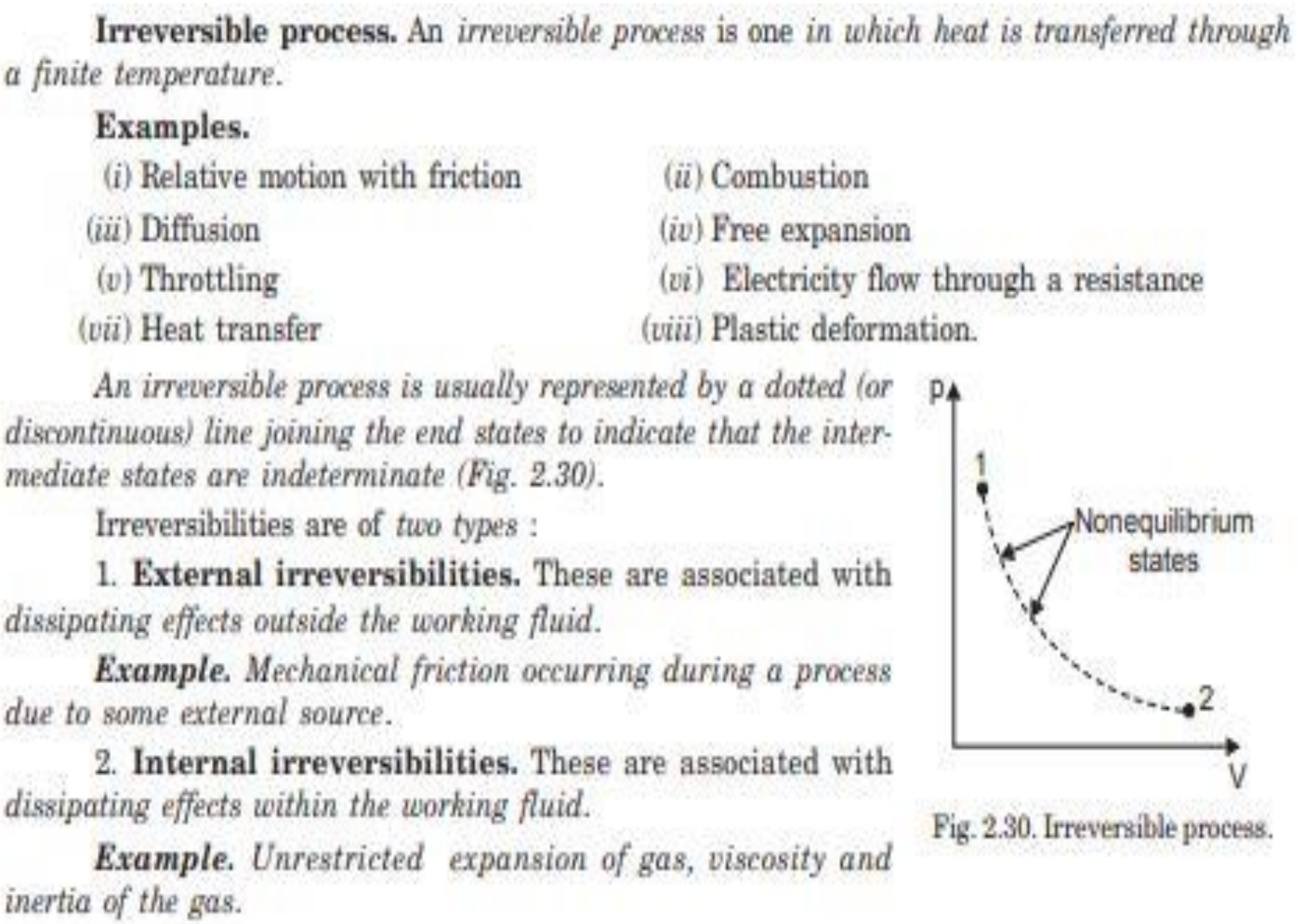
(*v*) Isothermal expansion or compression.

(*vi*) Electrolysis.

Reversible processes

- Isochoric process (V=Constant)
- Isobaric process (P = Constant)
- Isothermal Process (T = Constant ,PV=C)
- Adiabatic Process (Heat transfer Q = 0)
- Polytrophic Process

Irreversible Process



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. 2.30).

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.*

Fig. 2.30. Irreversible process.

ENERGY AND ITS FORMS

"Energy is usually defined as the ability to do mechanical work". It is indeed quite difficult to precisely define the "energy". We feel energy at every moment and can sense it very oftenly.

Another broader definition of energy says that "energy refers to the capacity for producing effects."

Energy can be classified in the following general categories;

(*a) Energy in transition: It refers to the energy that is in process of transition between substances or* regions because of some driving potential, such as difference or gradient of force, or of temperature, or of electrical potential etc. For example heat, work etc.

(*b) Energy stored in particular mass: It refers to the potential and kinetic energy associated with* masses that are elevated or moving with respect to the earth.

Apart from above broad classification the energy can also be categorised into various forms.

(*i) Macroscopic energy: It refers to the energy possessed by a system considered at macroscopic* level such as kinetic energy, potential energy etc.

(*ii) Microscopic energy: It refers to the energy defined at molecular level. Summation of energy* at molecular level or microscopic energy results in internal energy.

Some of the popular forms of energy are described below :

Potential energy: This type of energy is based on relative position of bodies in a system, i.e.

elevation in a gravitational field. Potential energy for a mass *m at elevation z is given as :*

P.E. = *m.g.z*

Here *g is the gravitational acceleration and elevation is measured from some reference point.*

Kinetic energy: It is based on the relative movement of bodies. For a mass m moving with certain

velocity *c it could be mathematically expressed as;*

K.E. = (1/2) *m.c2*

Internal energy: Internal energy of a system is the energy associated with the molecular

HEAT AND WORK

When two systems at different temperatures are brought into contact there are observable changes in some of their properties and changes continue till the two don't attain the same temperature if contact is prolonged. Thus, there is some kind of energy interaction at the boundary which causes change in temperatures. This form of energy interaction is called heat. *Thus 'heat' may be termed as the energy interaction at the system boundary which occurs due to temperature difference only. Heat is observable* in transit at the interface i.e. boundary, it can not be contained in a system. In general the heat transfer to the system is assigned with positive (+) sign while the heat transfer from the system is assigned with negative (–) sign. Its units are Calories.

In thermodynamics the work can be defined as follows:

"Work shall be done by the system if the total effect outside the system is equivalent to the raising of weight and this work shall be positive work".

In above definition the work has been defined as positive work and says that there need not be actual raising of weight but the effect of the system behaviour must be reducible to the raising of a weight and nothing else. Its units are N. m or Joule. Heat and work are two transient forms of energy.

3.1 Work Transfer

Work is one of the basic modes of energy transfer. In mechanics the action of a force on a moving body is identified as work. A force is a means of transmitting an effect from one body to another. But a force itself never produces a physical effect except when coupled with motion and hence it is not a form of energy. An effect such as the raising of a weight through a certain distance can be performed by using a small force through a large distance or a large force through a small distance. The product of force and distance is the same to accomplish the same effect. In mechanics work is defined as:

The work is done by a force as it acts upon a body moving in the direction of the force.

The action of a force through a distance (or of a torque through an angle) is called *mechanical work* since other forms of work can be identified, as discussed later. The product of the force and the distance moved parallel to the force is the magnitude of mechanical work.

In thermodynamics, work transfer is considered as occurring between the system and the surroundings. *Work is said to be done by a system if the sole effect on things external to the system can be reduced to the raising of a weight.* The weight may not actually be raised, but the net effect external to the system would be the raising of a weight. Let us consider the battery and the motor in Fig. 3.1 as a system. The motor is driving a fan. The system is doing work upon the surroundings. When the fan is replaced by a pulley and a weight, as shown in Fig. 3.2, the weight may be raised with the pulley driven by the motor. The sole effect on things external to the system is then the raising of a weight.

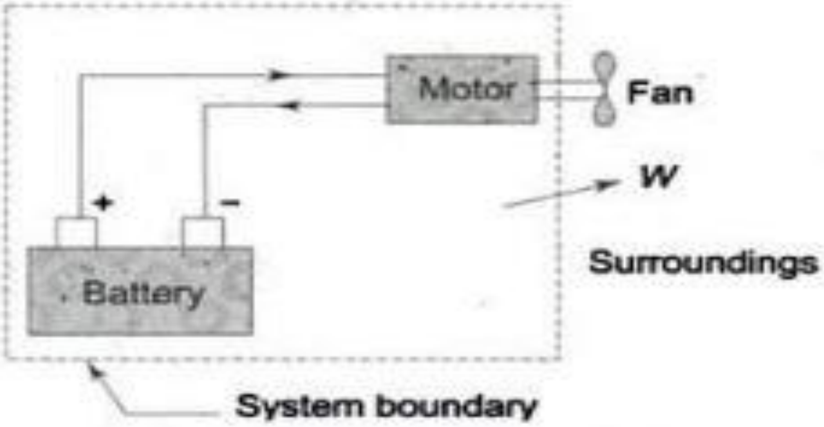
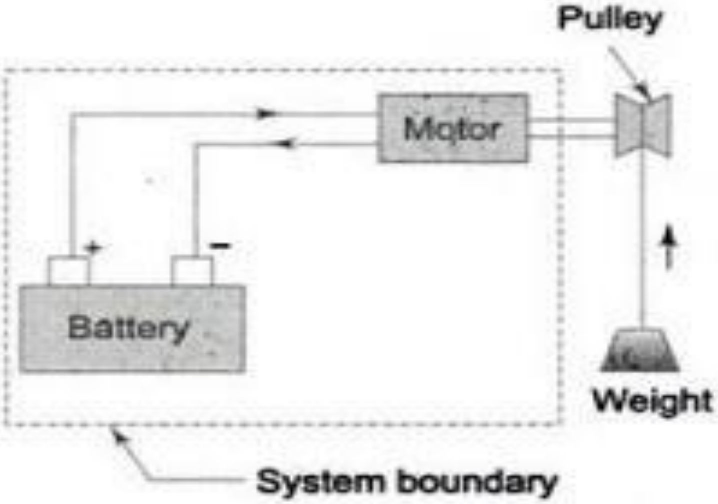


Fig. 3.1 *Battery-motor system driving a fan*



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 transfer which can get involved between them.

3.2 $p\mathrm{d}V$–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 significant only for equilibrium states. When the piston moves an infinitestimal distance $\mathrm{d}l$, 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

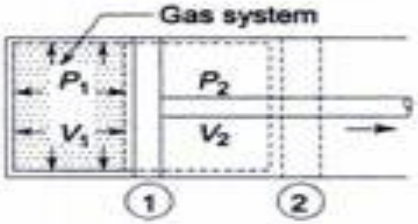


Fig. 3.4 *pdV work*

$$\text{đ}W = F \cdot \mathrm{d}l = pa\mathrm{d}l = p\mathrm{d}V \tag{3.1}$$

where $\mathrm{d}V = a\mathrm{d}l$ = infinitesimal displacement volume. The differential sign in $\mathrm{d}W$ 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

$$W_{1-2} = \int_{V_1}^{V_2} p\mathrm{d}V$$

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* $\int p\mathrm{d}V$ *can be performed only on a quasi-static path.*

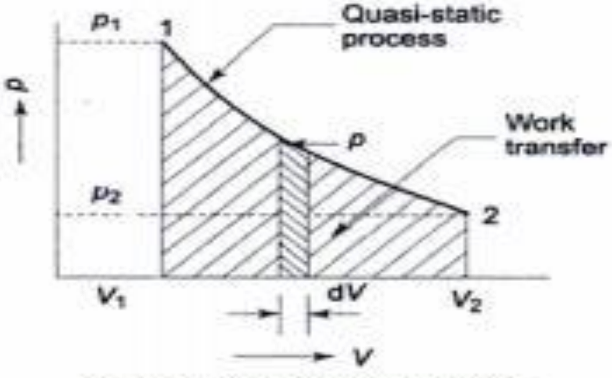


Fig. 3.5 *Quasi-static pdV work*

Displacement work in different thermodynamic processes

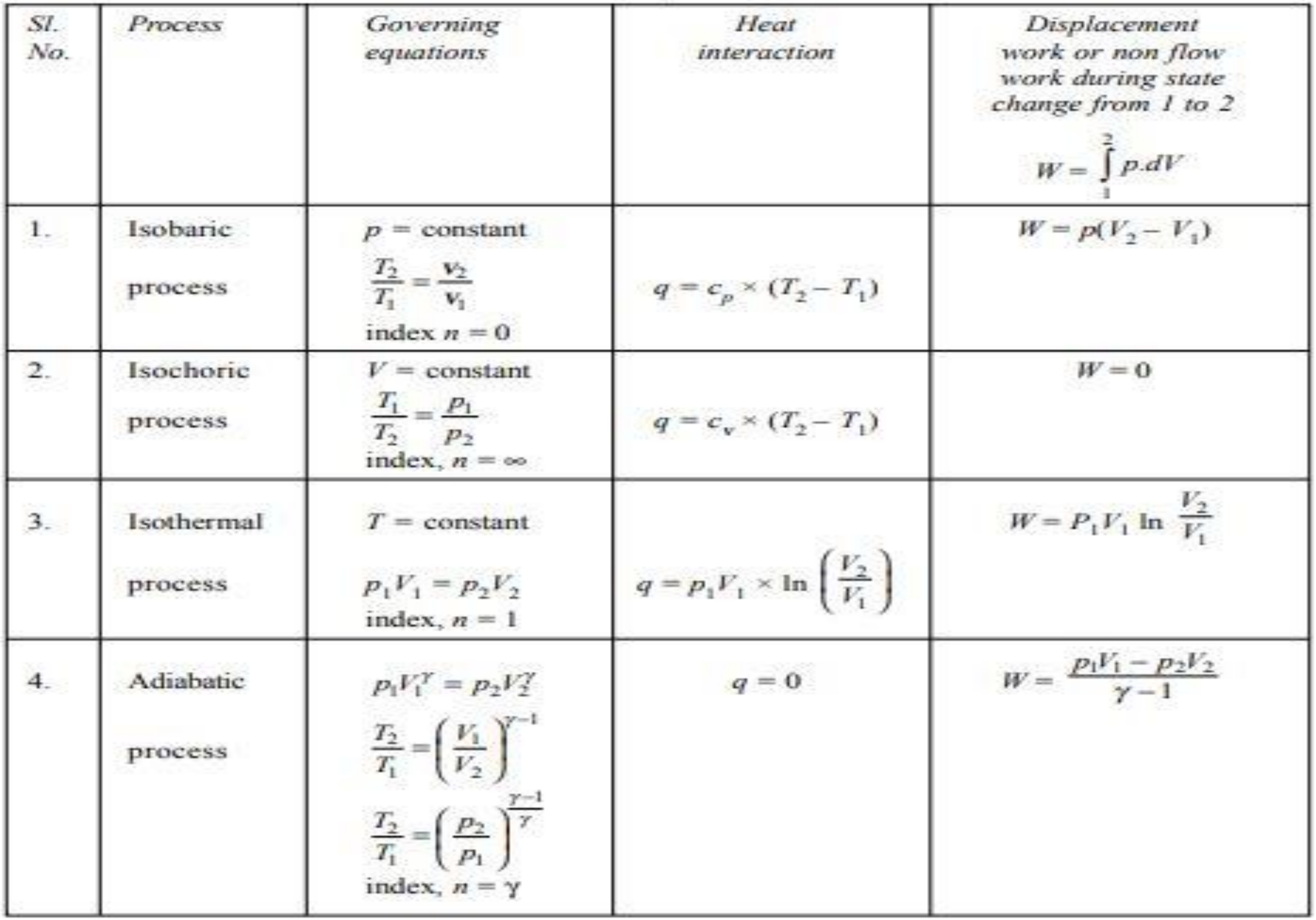


Table 3.1 *Thermodynamic processes*

Sl. No.	*Process*	*Governing equations*	*Heat interaction*	*Displacement work or non flow work during state change from 1 to 2* $W = \int_1^2 p.dV$
1.	Isobaric process	p = constant $\frac{T_2}{T_1} = \frac{V_2}{V_1}$ index $n = 0$	$q = c_p \times (T_2 - T_1)$	$W = p(V_2 - V_1)$
2.	Isochoric process	V = constant $\frac{T_1}{T_2} = \frac{p_1}{p_2}$ index, $n = \infty$	$q = c_v \times (T_2 - T_1)$	$W = 0$
3.	Isothermal process	T = constant $p_1V_1 = p_2V_2$ index, $n = 1$	$q = p_1V_1 \times \ln\left(\frac{V_2}{V_1}\right)$	$W = P_1V_1 \ln \frac{V_2}{V_1}$
4.	Adiabatic process	$p_1V_1^{\gamma} = p_2V_2^{\gamma}$ $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ $\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$ index, $n = \gamma$	$q = 0$	$W = \frac{p_1V_1 - p_2V_2}{\gamma - 1}$

5.	Polytropic process	$p_1V_1^n = p_2V_2^n$ $\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{n-1}$ $\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}$ $C_n = c_v\left(\frac{\gamma - n}{1 - n}\right)$ where C_n is specific heat for polytropic process.	$q = c_v\left(\frac{\gamma - n}{1 - n}\right)$ $\times (T_2 - T_1)$ or, $q = \left(\frac{\gamma - n}{\gamma - 1}\right)$ × work	$W = \frac{p_1V_1 - p_2V_2}{n - 1}$
6.	Hyperbolic process	pV = constant but not necessarily T = constant	$q = c_v\,(T_2 - T_1)$ $+ RT_1 \ln\left(\frac{V_2}{V_1}\right)$	$W = RT_1 \ln\left(\frac{V_2}{V_1}\right)$
7.	Free expansion in adiabatic conditions	Unresisted expansion	$q = 0$	$W = 0$

3.3 NON-FLOW WORK AND FLOW WORK

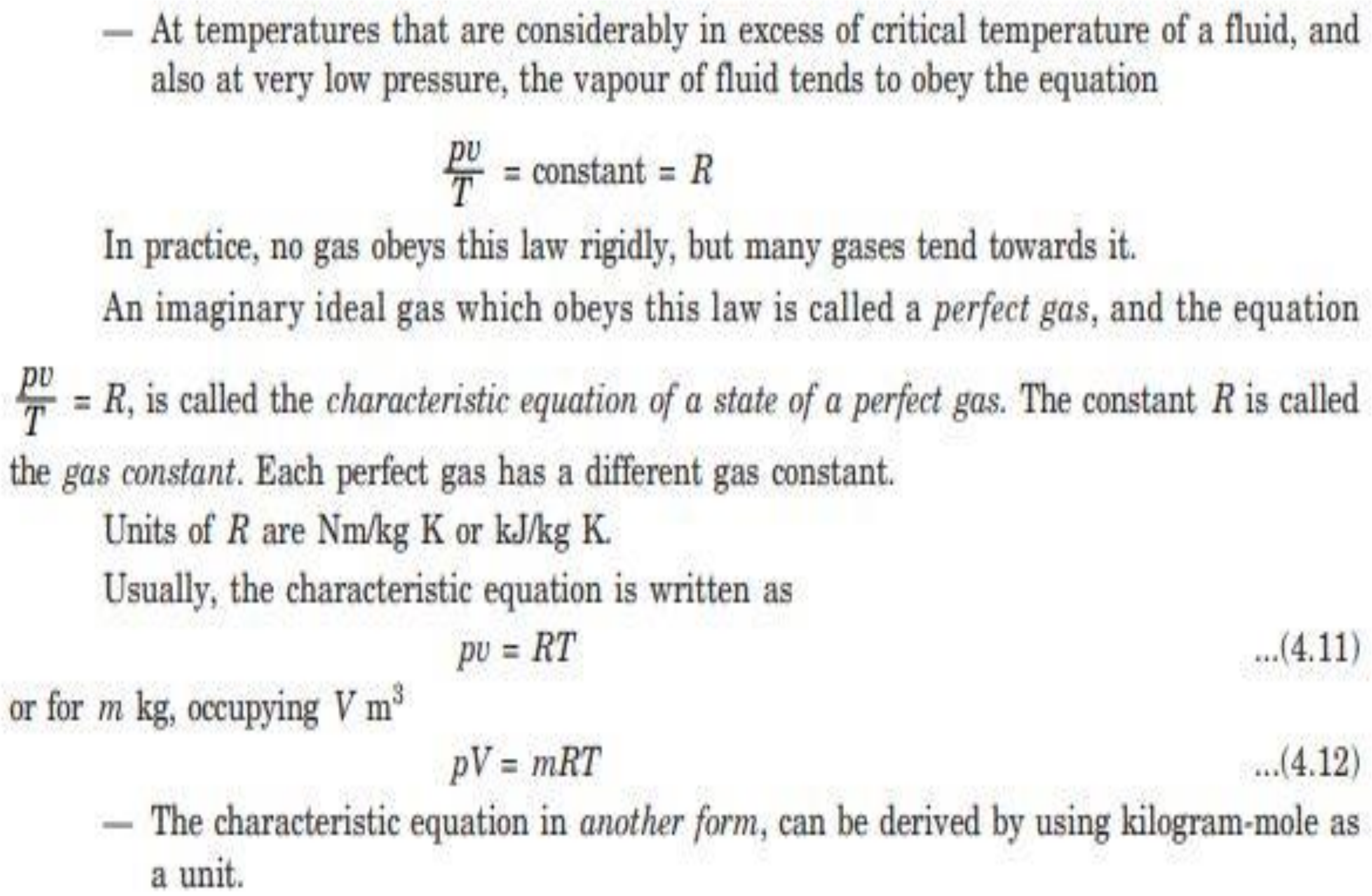
Work interaction taking place in a system can be classified as flow work or non-flow work based on the nature of process.

Two basic types of processes are

(*i*) Flow process

(*ii*) Non flow process

Ideal and Real gases



— 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

$$pv = RT \quad \text{...(4.11)}$$

or for m kg, occupying V m^3

$$pV = mRT \quad \text{...(4.12)}$$

— 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

$$m = nM \qquad \text{...(4.13)}$$

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. (4.13) in eqn. (4.12) 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

$$pV = nR_0T \qquad \text{...(4.14)}$$

Since $MR = R_0$, then

$$R = \frac{R_0}{M} \qquad \text{...(4.15)}$$

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 m^3.

Therefore from eqn. (4.14),

$$R_0 = \frac{pV}{nT} = \frac{1 \times 10^5 \times 22.71}{1 \times 273.15}$$

$$= 8314.3 \text{ Nm/mole K}$$

Using eqn. (4.15), 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

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

4.8.3. 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., $$u = f(T)$$

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

According to non-flow energy equation,

$$dQ = du + dW$$

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

$$\therefore \quad dQ = du$$

At constant volume for a perfect gas, from eqn. (4.17), for 1 kg

$$dQ = c_v dT$$

$$\therefore \quad dQ = du = c_v dT$$

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

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 ...(4.20)

or For mass m, of a perfect gas

Internal energy, $U = mc_v T$ ...(4.21)

For a perfect gas, in any process between states 1 and 2, we have from Eqn. (4.21)

Gain in internal energy,

$$U_2 - U_1 = mc_v (T_2 - T_1) \quad ...(4.22)$$

Eqn. (4.22) gives the gains of internal energy for a perfect gas between two states *for any process, reversible* or *irreversible.*

4.8.4. 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,

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

$$= mR(T_2 - T_1) \qquad \left[\begin{array}{l} \because \; p_1V_1 = mRT_1 \\ \quad p_2V_2 = mRT_2 \\ \qquad p_1 = p_2 = p \text{ in this case} \end{array}\right]$$

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

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

$$\therefore \qquad c_v + R = c_p$$

or

$$c_p - c_v = R \qquad \text{...(4.23)}$$

Dividing both sides by c_v, we get

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

$$\therefore \qquad c_v = \frac{R}{\gamma - 1} \qquad \text{...[4.23 (a)]}$$

(where $\gamma = c_p/c_v$)

Similarly, dividing both sides by c_p, we get

$$c_p = \frac{\gamma R}{\gamma - 1} \qquad \text{...[4.23 (b)]}$$

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

Dalton's law of partial pressures states that the "total pressure of a mixture of gases is equal to the sum of partial pressures of constituent gases." Partial pressure of each constituent can be defined as the pressure exerted by the gas if it alone occupied the volume at the same temperature.

Thus, for any mixture of gases having 'j' gases in it, the mathematical statement of Dalton's law says,

$$p = p_1 + p_2 + p_3 + \ldots\ldots + p_j$$

if $$V = V_1 = V_2 = V_3 = \ldots\ldots = V_j$$

and $$T = T_1 = T_2 = T_3 = \ldots\ldots\ T_j$$

Dalton's law can be applied to both mixture of real gases and ideal gases.

$$(a)\ \boxed{\begin{matrix} m_1, p_1 \\ V, T \end{matrix}} + \boxed{\begin{matrix} m_2, p_2 \\ V, T \end{matrix}} \rightarrow \boxed{\begin{matrix} m, p \\ V, T \end{matrix}} \qquad (b)\ \boxed{\begin{matrix} m_1, V_1 \\ p, T \end{matrix}} + \boxed{\begin{matrix} m_2, V_2 \\ p, T \end{matrix}} \rightarrow \boxed{\begin{matrix} m, V \\ p, T \end{matrix}}$$

constituent gases Mixture

Fig. 1.11 *(a) Dalton's law of partial pressures, (b) Amagat's law*

Let us take mixture of any three, perfect gases, say, 1, 2, 3 in a container having volume 'V' and temperature T.

Equation of state for these gases shall be,

$$p_1 V = m_1 R_1 T\ ;\ p_2\ V = m_2 \cdot R_2 \cdot T,\ p_3 V = m_3 \cdot R_3 \cdot T$$

The partial pressures of three gases shall be,

$$p_1 = \frac{m_1 R_1 T}{V},\ p_2 = \frac{m_2 \cdot R_2\ T}{V},\ p_3 = \frac{m_3 \cdot R_3 \cdot T}{V}$$

From Dalton's law;

$$p = p_1 + p_2 + p_3 = (m_1 R_1 + m_2 R_2 + m_3 R_3) \cdot \frac{T}{V}$$

or, it can be given in general form as,

$$pV = T \cdot \sum_{i=1}^{j} m_i \cdot R_i$$

where i refers to constituent gases

Amagat's law of additive volumes states that volume of a gas mixture is equal to the sum o volumes each gas would occupy at the mixture pressure and temperature.

$$V = V_1 + V_2 + V_3 \ldots\ldots\ldots + V_j$$

$$p = p_1 = p_2 = p_3 \ldots\ldots\ldots p_j$$

$$T = T_1 = T_2 = T_3 = \ldots\ldots\ldots T_j$$

Mass balance upon mixture yields $m = m_1 + m_2 + m_3$

or

$$m = \sum_{i=1}^{j} m_i$$

From above the gas constant for the mixture can be given as;

$$R = \frac{m_1 R_1 + m_2 R_2 + m_3 R_3}{(m_1 + m_2 + m_3)}$$

or, in general form,

$$R = \frac{\sum_{i=1}^{j} m_i \cdot R_i}{\sum_{i=1}^{j} m_i}$$

Mole fraction x_i of a constituent gas can be defined as the ratio of number of moles of tha constituent to the total number of moles of all constituents.

Thus mole fractions of three gases, if number of moles of three gases are n_1, n_2 and n_3;

$$x_1 = \frac{n_1}{n_1 + n_2 + n_3}$$

$$x_2 = \frac{n_2}{n_1 + n_2 + n_3}$$

$$x_3 = \frac{n_3}{n_1 + n_2 + n_3}$$

or, in general $x_i = \dfrac{n_i}{\sum n_i}$

Total no. of moles,

$$n = n_1 + n_2 + n_3 \text{ or, } n = \sum_{i=1}^{j} n_i$$

Sum of mole fractions of all constituent equals to 1,

$$\sum x_i = \frac{\sum n_i}{n} = 1$$

Number of moles of any constituent gas,

$$n_i = n \cdot x_i$$

For M_i being the molecular weight of a constituent gas, the mass m_i of that constituent shall be

$$m_i = n_i \cdot M_i$$

or, $$m_i = n \cdot x_i \cdot M_i$$

and the total mass m, shall be

$$m = \sum m_i = n. \sum x_i \cdot M_i$$

Molecular weight of mixture shall be:

$$M = \frac{m}{n} = \sum x_i \cdot M_i$$

1.16 REAL GAS

When a gas is found to disobey the perfect gas law, i.e. the equation of state for ideal gas, then it is called 'real gas'. Real gas behaviour can also be shown by a perfect gas at the changed thermodynamic states such as high pressure etc.

Deviation of real gas from ideal gas necessitates the suitable equation of state which can be used for interrelating the thermodynamic properties P, V, and T.

From the kinetic theory of gases it is obvious that the ideal gas equation of state suits the gas behaviour when intermolecular attraction and volume occupied by the molecules themselves is negligibly small in reference to gas volume. At high pressures intermolecular forces and volume of molecules both increase and so the gas behaviour deviates from ideal gas to real gas.

A number of mathematical equations of state suggested by Van der-Waals, Berthelot, Dieterici, Redlich-Kwong, Beattie-Bridgeman and Martin-Hou etc. are available for analysing the real gas behaviour.

Dalton's law and Amagat's law can also be used for real gases with reasonable accuracy in conjunction with modified equations of state.

As the ideal gas equation does not conform to the real gas behaviour in certain ranges of pressures and temperatures, so the perfect gas equation should be modified using compressibility factor for the gas at given pressure and temperature.

Such modified form of equations shall be;

$$P\overline{v} = Z \cdot \overline{R} \cdot T$$

Here Z is the compressibility factor, a function of pressure and temperature.

Thus, compressibility factor is like a correction factor introduced in ideal equation of state for suiting the real gas behaviour. Compressibility factor is an indication of deviation of a gas from ideal gas behaviour and can be mathematically given as;

$$Z = f(P, T)$$

or $$Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}}$$

Here, $v_{\text{ideal}} = \frac{RT}{P}$ i.e. $Z = 1$ for ideal gases while Z can be greater than or less than unity.

Individual graphical representations are available for getting the compressibility factor as shown in Fig 1.12. Compressibility factor charts are available for different substances. Compressibility factors for various substances can also be shown on a generalized compressibility chart using reduced properties. Reduced properties are non-dimensional properties given as ratio of existing property to critical property of substance. Such as reduced pressure is ratio of pressure of gas to critical pressure of gas. Similarly, reduced temperature can be given by ratio of temperature of gas to critical temperature of gas.

Reduced pressure, $$p_R = \frac{p}{p_c}$$

Reduced temperature, $$T_R = \frac{T}{T_c}$$

1.17 VANDER' WAALS AND OTHER EQUATIONS OF STATE FOR REAL GAS

Vander' Waals suggested the equation of state for real gas in 1873. The equation has been obtained applying the laws of mechanics at molecular level and introducing certain constants in the equation of state for ideal gas. This equation agrees with real gas behaviour in large range of gas pressures and temperatures.

Vander' Waals equation of state for real gas is as follows,

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = \bar{R}T$$

where 'a' is the constant to take care of the mutual attraction amongst the molecules and thus $\left(\frac{a}{\bar{v}^2}\right)$ accounts for cohesion forces.

***Table 1.6** Vander' Waals constant*

Gas	*Constant a, $N.m^4/(kg.\ mol)^2$*	*Constant b, $m^3/kg.mol$*
Helium	34176.2×10^2	2.28×10^{-2}
Hydrogen	251.05×10^2	2.62×10^{-2}
Oxygen	1392.5×10^2	3.14×10^{-2}
Air	1355.22×10^2	3.62×10^{-2}
Carbon dioxide	3628.50×10^2	3.14×10^{-2}

Constant '*b*' accounts for the volumes of molecules which are neglected in perfect gas equation, thus it denotes "co-volume", Mathematically,

$$a = \frac{27\bar{R}^2 T_c^2}{64 p_c}, \quad b = \left(\bar{R} T_c\right) / \left(8 p_c\right)$$

Here, p_c, T_c are critical point pressures and temperatures having values as given in appendix.

Thus these constants '*a*' & '*b*' are determined from behaviour of substance at the critical point.

In general it is not possible to have a single equation of state which conforms to the real gas behaviour at all pressures and temperatures.

Zeroth ‘Law of thermodynamics

Zeroth law of thermodynamics states that if the bodies A and B are in thermal equilibrium with a third body C separately then the two bodies A and B shall also be in thermal equilibrium with each other. This is the principle of temperature measurement. Block diagram shown in Fig. 2.1*a and 2.1b* show the zeroth law of thermodynamics and its application for temperature measurement.

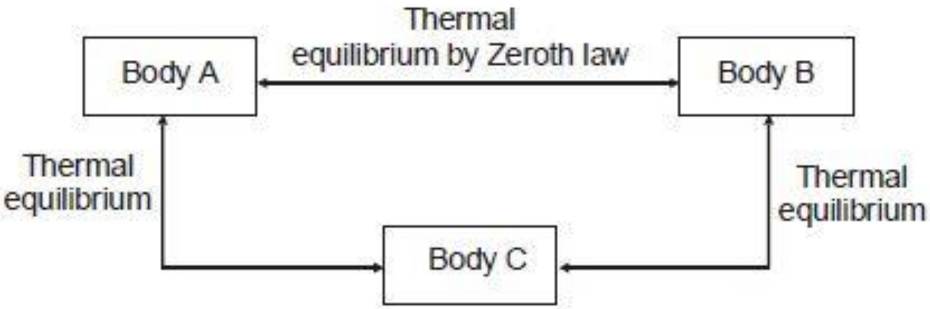


Fig. Zeroth law of thermodynamics

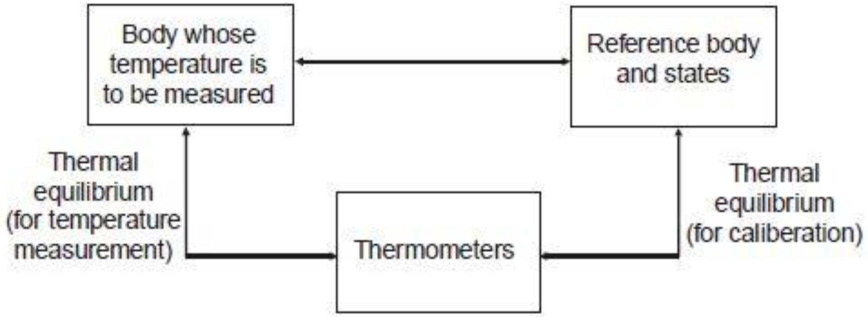


Fig. Application of Zeroth law of thermodynamics

Temperature:- Temperature is a property of a system , which tells the hotness and coldness of a system.

Temperatures scales

There are different types of scales of temperature

(1). Celsius scale or centigrade scale (ºC)

Anders Celsius gave this Celsius or Centigrade scale using ice point of 0°C as the lower fixed point and steam point of 100ºC as upper fixed point for developing the scale. It is denoted by letter *C.*

(2). Fahrenheit Scale (F)

Fahrenheit gave another temperature scale known as Fahrenheit scale and has the lower fixed point as 32 F and the upper fixed point as 212 F. The interval between these two is equally divided into 180 part. It is denoted by letter F. Each part represents 1 F.

(3). Rankine scale (*R*)

Rankine scale was developed by William John MacQuorn Rankine, a Scottish engineer. It is denoted by letter *R. It is related to Fahrenheit scale as given below.*

$$TR = TF + 459.67$$

(4). Kelvin scale (K)

Kelvin scale proposed by Lord Kelvin is very commonly used in thermodynamic analysis. It also defines the absolute zero temperature. Zero degree Kelvin or absolute zero temperature is taken as –273.15ºC. It is denoted by letter K.

Different temperature scales

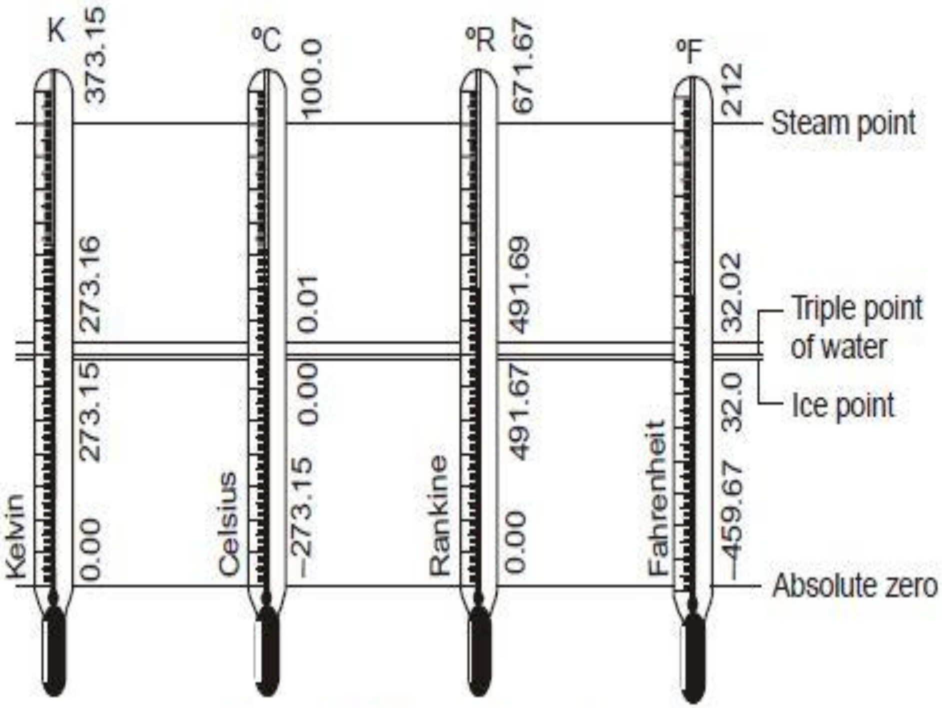


Fig. 2.2 Different temperature scales

Detailed discussion on Kelvin scale has been done in chapter 4 along with absolute thermodynamic temperature scale. Mathematically, it is related to the different temperature scales as follows,

$$\frac{T_C}{100} = \frac{T_F - 32}{180} = \frac{T_K - 273.15}{100} = \frac{T_R - 491.67}{180}$$

$$\frac{T_K}{100} = \frac{T_R}{180}$$

Temperature measurement

Thermometers are generally used to measure the temperature of a system. Different types of thermometers are given below:

(1). **Liquid Thermometer**

(2). Gas Thermometers

- **(i) .** ***Constant volume gas thermometer***
- ***(ii). Constant pressure gas thermometer***

(3). Electrical resistance thermometer

(4). Thermoelectric Thermometer

Application of first law of thermodynamic to different processes

(a). Constant volume processes or isochoric process

(b). Constant pressure process or isobaric process

(c). Isothermal process

(d). Adiabatic process

(e). Polytrophic process

First law of thermodynamics for closed system

First law of thermodynamic for close system can be classified in to two parts

(1). Closed system following a process

(2). Closed system following a cycle

First law for a cyclic process

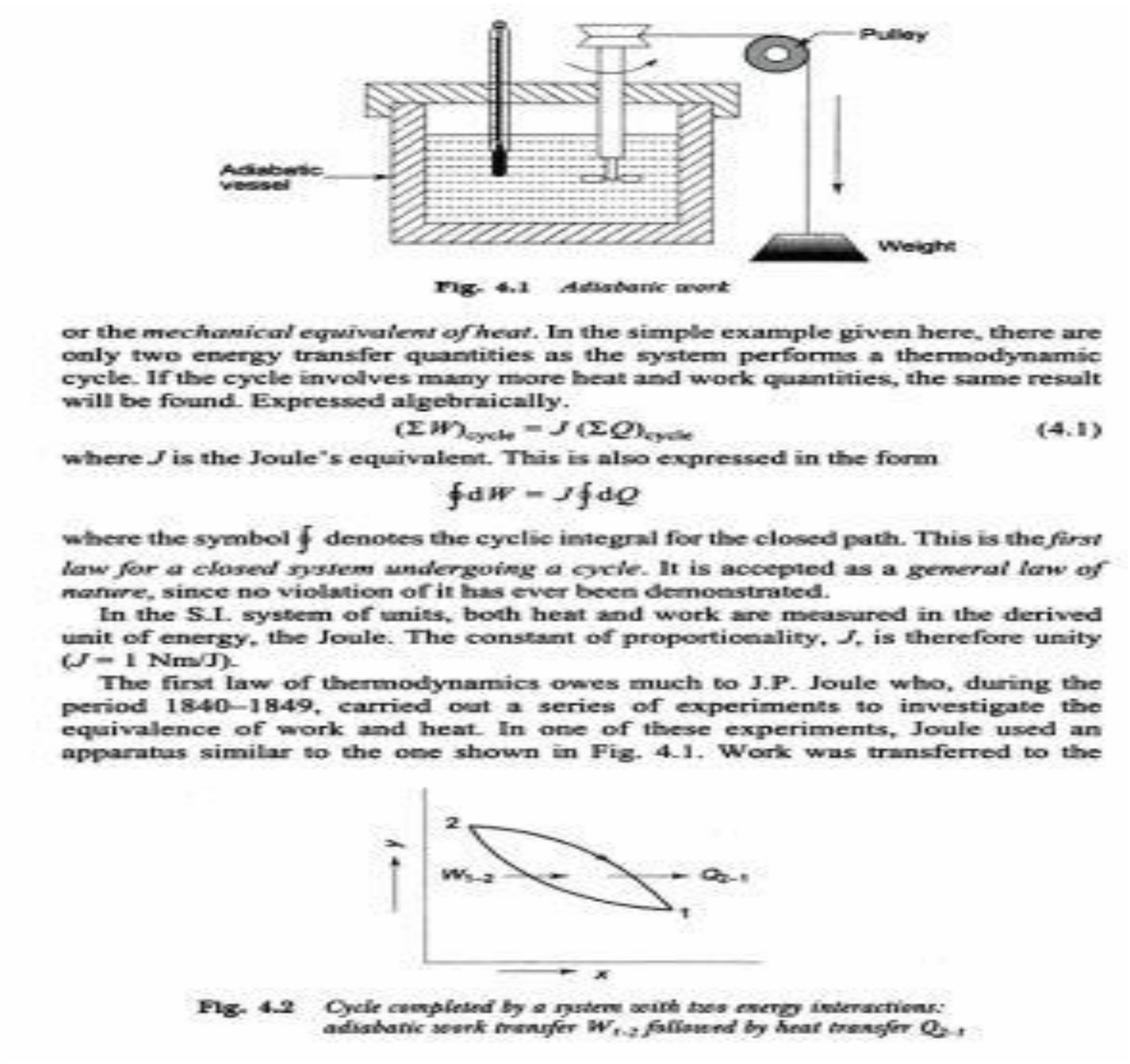


Fig. 4.1 *Adiabatic work*

or the *mechanical equivalent of heat*. In the simple example given here, there are only two energy transfer quantities as the system performs a thermodynamic cycle. If the cycle involves many more heat and work quantities, the same result will be found. Expressed algebraically,

$$(\Sigma W)_{\text{cycle}} = J\,(\Sigma Q)_{\text{cycle}} \tag{4.1}$$

where J is the Joule's equivalent. This is also expressed in the form

$$\oint \mathrm{d}W = J \oint \mathrm{d}Q$$

where the symbol $\oint$ denotes the cyclic integral for the closed path. This is the *first law for a closed system undergoing a cycle*. It is accepted as a *general law of nature*, since no violation of it has ever been demonstrated.

In the S.I. system of units, both heat and work are measured in the derived unit of energy, the Joule. The constant of proportionality, J, is therefore unity ($J = 1$ Nm/J).

The first law of thermodynamics owes much to J.P. Joule who, during the period 1840–1849, carried out a series of experiments to investigate the equivalence of work and heat. In one of these experiments, Joule used an apparatus similar to the one shown in Fig. 4.1. Work was transferred to the

Fig. 4.2 *Cycle completed by a system with two energy interactions: adiabatic work transfer W_{1-2} followed by heat transfer Q_{2-1}*

measured mass of water by means of a paddle wheel driven by the falling weight. The rise in the temperature of water was recorded. Joule also used mercury as the fluid system, and later a solid system of metal blocks which absorbed work by friction when rubbed against each other. Other experiments involved the supplying of work in an electric current. In every case, he found the same ratio (J) between the amount of work and the quantity of heat that would produce identical effects in the system.

Prior to Joule, heat was considered to be an invisible fluid flowing from a body of higher calorie to a body of lower calorie, and this was known as the *caloric theory of heat*. It was Joule who first established that heat is a form of energy, and thus laid the foundation of the first law of thermodynamics.

4.2 First Law for a Closed System Undergoing a Change of State

The expression $(\Sigma W)_{\text{cycle}} = (\Sigma Q)_{\text{cycle}}$ applies only to systems undergoing cycles, and the algebraic summation of all energy transfer across system boundaries is zero. But if a system undergoes a change of state during which both heat transfer and work transfer are involved, the *net* energy transfer will be stored or accumulated within the system. If Q is the amount of heat transferred to the system and W is the amount of work transferred from the system during the process (Fig. 4.3), the net energy transfer ($Q - W$) will be stored in the system. Energy in storage is neither heat nor work, and is given the name *internal energy* or simply, the *energy* of the system.

Therefore $$Q - W = \Delta E$$

where ΔE is the increase in the energy of the system

or $$Q = \Delta E + W \tag{4.2}$$

Here Q, W, and ΔE are all expressed in the same units (in joules). Energy may be stored by a system in different modes, as explained in Article 4.4.

If there are more energy transfer quantities involved in the process, as shown in Fig. 4.4, the first law gives

$$(Q_2 + Q_3 - Q_1) = \Delta E + (W_2 + W_3 - W_1 - W_4)$$

Fig. 4.3 *Heat and work interactions of a system with its surroundings in a process*

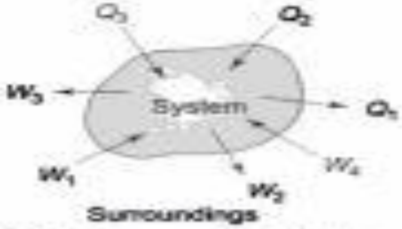


Fig. 4.4 *System-surroundings interaction in a process involving many energy fluxes*

Energy is thus conserved in the operation. The first law is a particular formulation of the principle of the conservation of energy. Equation (4.2) may also be considered as the definition of energy. This definition does not give an absolute value of energy E, but only the change of energy ΔE for the process. It can, however, be shown that the energy has a definite value at every state of a system and is, therefore, a property of the system.

4.3 Energy—A Property of the System

Consider a system which changes its state from state 1 to state 2 by following the path A, and returns from state 2 to state 1 by following the path B (Fig. 4.5). So the system undergoes a cycle. Writing the first law for path A

$$Q_A = \Delta E_A + W_A \tag{4.3}$$

and for path B

$$Q_B = \Delta E_B + W_B \tag{4.4}$$

The processes A and B together constitute a cycle, for which

$$(\Sigma W)_{\text{cycle}} = (\Sigma Q)_{\text{cycle}}$$

or

$$W_A + W_B = Q_A + Q_B$$

or

$$Q_A - W_A = W_B - Q_B \tag{4.5}$$

From equations (4.3), (4.4), and (4.5), it yields

$$\Delta E_A = -\Delta E_B \tag{4.6}$$

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

$$\Delta E_A = -\Delta E_C \tag{4.7}$$

From equations (4.6) and (4.7)

$$\Delta E_B = \Delta E_C \tag{4.8}$$

Therefore, 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*.

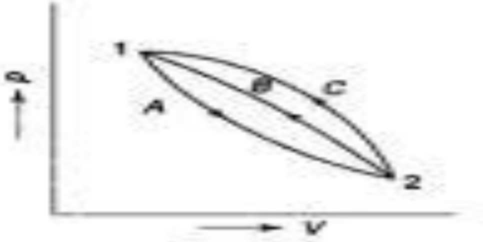


Fig. 4.5 *Energy—a property of a system*

The energy E is an extensive property. The *specific energy*, $e = E/m$ (J/kg), is an intensive property.

The cyclic integral of any property is zero, because the final state is identical with the initial state. $\oint dE = 0$, $\oint dV = 0$, etc. So for a cycle, the equation (4.2) reduces to equation (4.1).

4.4 Different Forms of Stored Energy

The symbol E refers to the total energy stored in a system. Basically there are two modes in which energy may be stored in a system:

(a) Macroscopic energy mode
(b) Microscopic energy mode

The macroscopic energy mode includes the macroscopic kinetic energy and potential energy of a system. Let us consider a fluid element of mass m having the centre of mass velocity $\bar{V}$ (Fig. 4.6). The macroscopic kinetic energy E_K of the fluid element by virtue of its motion is given by

$$E_K = \frac{m\bar{V}^2}{2}$$

If the elevation of the fluid element from an arbitrary datum is z, then the macroscopic potential energy E_P by virtue of its position is given by

$$E_P = mgz$$

The microscopic energy mode refers to the energy stored in the molecular and atomic structure of the system, which is called the *molecular internal energy* or *simply internal energy*, customarily denoted by the symbol U. Matter is composed of molecules. Molecules are in random thermal motion (for a gas) with an average velocity $\bar{v}$, constantly colliding with one another and with the walls (Fig. 4.6). Due to a collision, the molecules may be subjected to rotation as well

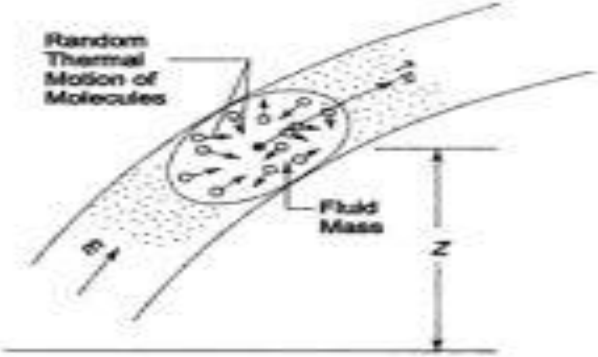


Fig. 4.6 *Macroscopic and microscopic energy*

as vibration. They can have translational kinetic energy, rotational kinetic energy, vibrational energy, electronic energy, chemical energy and nuclear energy (Fig. 4.7). If ε represents the energy of one molecule, then

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{chem}} + \varepsilon_{\text{electronic}} + \varepsilon_{\text{nuclear}} \tag{4.9}$$

If N is the total number of molecules in the system, then the total internal energy

$$U = N\varepsilon \tag{4.10}$$

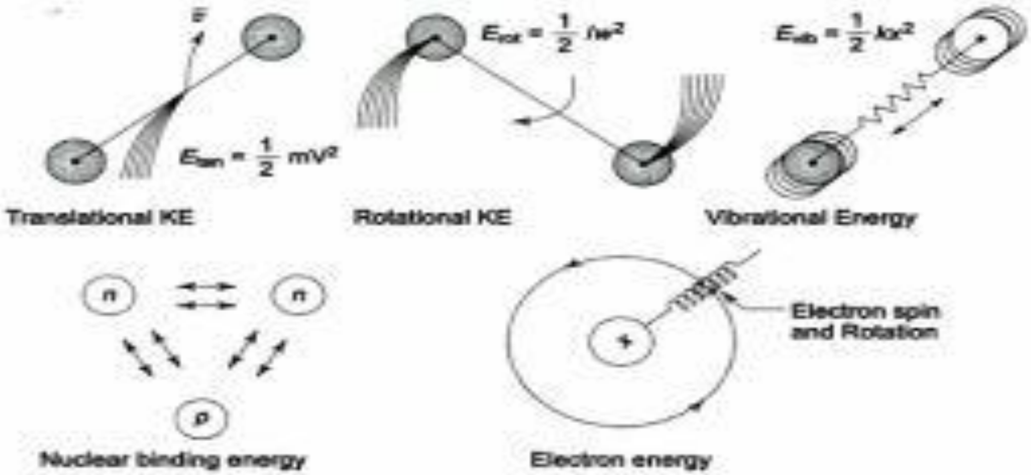


Fig. 4.7 *Various components of internal energy stored in a molecule*

In an ideal gas there are no intermolecular forces of attraction and repulsion, and the internal energy depends only on temperature. Thus

$$U = f(T) \text{ only} \tag{4.11}$$

for an ideal gas

Other forms of energy which can also be possessed by a system are magnetic energy, electrical energy and surface (tension) energy. In the absence of these forms, the total energy E of a system is given by

$$E = \underbrace{E_K + E_P}_{\text{macro}} + \underbrace{U}_{\text{micro}} \tag{4.12}$$

where E_K, E_P, and U refer to the kinetic, potential and internal energy, respectively. In the absence of motion and gravity

$$E_K = 0, E_P = 0$$

$$E = U$$

and equation (4.2) becomes

$$Q = \Delta U + W \tag{4.13}$$

U is an extensive property of the system. The specific internal energy u is equal to U/m and its unit is J/kg.

In the differential forms, equations (4.2) and (4.13) become

$$\text{đ}Q = \mathrm{d}E + \text{đ}W \tag{4.14}$$

$$\text{đ}Q = \text{đ}U + \text{đ}W \tag{4.15}$$

where $\text{đ}W = \text{đ}W_{pdV} + \text{đ}W_{\text{shaft}} + \text{đ}W_{\text{electrical}} + \ldots,$

considering the different forms of work transfer which may be present. When only $p\mathrm{d}V$ work is present, the equations become

$$\text{đ}Q = \mathrm{d}E + p\mathrm{d}V \tag{4.16}$$

$$\text{đ}Q = \mathrm{d}U + p\mathrm{d}V \tag{4.17}$$

or, in the integral form

$$Q = \Delta E + \int p\mathrm{d}V \tag{4.18}$$

$$Q = \Delta U + \int p\mathrm{d}V \tag{4.19}$$

4.5 Specific Heat at Constant Volume

The specific heat of a substance at constant volume c_v is defined as the rate of change of specific internal energy with respect to temperature when the volume is held constant, i.e.

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \tag{4.20}$$

For a constant-volume process

$$(\Delta u)_v = \int_{T_1}^{T_2} c_v \cdot \mathrm{d}T \tag{4.21}$$

The first law may be written for a closed stationary system composed of a unit mass of a pure substance

$$Q = \Delta u + W$$

or

$$\text{đ}Q = \mathrm{d}u + \text{đ}W$$

For a process in the absence of work other than $p\mathrm{d}V$ work

$$\text{đ}W = p\,\text{đ}V$$

$\therefore$

$$\text{đ}Q = \mathrm{d}u + p\mathrm{d}v \tag{4.22}$$

When the volume is held constant

$$(Q)_v = (\Delta u)_v$$

$\therefore$

$$(Q)_v = \int_{T_1}^{T_2} c_v\,\mathrm{d}T \tag{4.23}$$

Heat transferred at constant volume increases the internal energy of the system.

If the specific heat of a substance is defined in terms of heat transfer, then

$$c_v = \left(\frac{\partial Q}{\partial T}\right)_v$$

Since Q is not a property, this definition does not imply that c_v is a property of a substance. Therefore, this is not the appropriate method of defining the specific heat, although $(dQ)_v = du$.

Since u, T, and v are properties, c_v is a property of the system. The product $mc_v = C_v$ is called the *heat capacity at constant volume* (J/K).

4.6 Enthalpy

The enthalpy of a substance, h, is defined as

$$h = u + pv \tag{4.24}$$

It is an intensive property of a system (kJ/kg).

Internal energy change is equal to the heat transferred in a constant volume process involving no work other than pdV work. From equation (4.22), it is possible to derive an expression for the heat transfer in a constant pressure process involving no work other than pdV work. In such a process in a closed stationary system of unit mass of a pure substance

$$đQ = du + pdv$$

At constant pressure

$$pdv = d(pv)$$

$$\therefore \quad (đQ)_p = du + d(pv)$$

or

$$(đQ)_p = d(u + pv)$$

or

$$(đQ)_p = dh \tag{4.25}$$

where $h = u + pv$ is the *specific enthalpy*, a property of the system.

Heat transferred at constant pressure increases the enthalpy of a system.

For an ideal gas, the enthalpy becomes

$$h = u + RT \tag{4.26}$$

Since the internal energy of an ideal gas depends only on the temperature (Eq. 4.11), the enthalpy of an ideal gas also depends on the temperature only, i.e.

$$h = f(T) \text{ only} \tag{4.27}$$

Total enthalpy $H = mh$

Also

$$H = U + pV$$

and

$$h = H/m \text{ (J/kg)}$$

4.7 Specific Heat at Constant Pressure

The specific heat at constant pressure c_p is defined as the rate of change of enthalpy with respect to temperature when the pressure is held constant

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p \tag{4.28}$$

Since h, T and p are properties, so c_p is a property of the system. Like c_v, c_p should not be defined in terms of heat transfer of constant pressure, although $(\mathrm{d}Q)_p = \mathrm{d}h$.

For a constant pressure process

$$(\Delta h)_p = \int_{T_1}^{T_2} c_p \cdot \mathrm{d}T \tag{4.29}$$

The first law for a closed stationary system of unit mass

$$\text{đ}Q = \mathrm{d}u + p\mathrm{d}v$$

Again

$$h = u + pv$$

$\therefore$

$$\mathrm{d}h = \mathrm{d}u + p\mathrm{d}V + v\mathrm{d}p$$
$$= \mathrm{d}Q + v\mathrm{d}p$$

$\therefore$

$$\text{đ}Q = \mathrm{d}h - v\mathrm{d}p \tag{4.30}$$

$\therefore$

$$(\text{đ}Q)_p = \mathrm{d}h$$

or

$$(Q)_p = (\Delta h)_p$$

$\therefore$ From equations (4.19) and (4.20)

$$(Q)_p = \int_{T_1}^{T_2} c_p\,\mathrm{d}T$$

c_p is a property of the system, just like c_v. The *heat capacity at constant pressure* C_p is equal to mc_p (J/K).

4.8 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, $\text{đ}Q = 0$, $\text{đ}W = 0$.

The first law gives

$$\mathrm{d}E = 0$$

or

$$E = \text{constant}$$

The energy of an isolated system is always constant.

4.9 Perpetual Motion Machine of the First Kind–PMM1

The first law states the general principle of the conservation of energy. *Energy is neither created nor destroyed, but only gets transformed from one form to another*. There can be no machine which would continuously supply mechanical work without some other form of energy disappearing simultaneously (Fig. 4.8). Such a *fictitious machine* is called a *perpetual motion machine of the first kind*, or in brief, PMM1. *A PMM1 is thus impossible.*

Example 4.2 When a system is taken from state *a* to state *b*, in Fig. Ex. 4.2, along path *acb*, 84 kJ of heat flow into the system, and the system does 32 kJ of work. (a) How much will the heat that flows into the system along path *adb* be, if the work done is 10.5 kJ? (b) When the system is returned from *b* to *a* along the curved path, the work done on the system is 21 kJ. Does the system absorb or liberate heat, and how much of the heat is absorbed or liberated? (c) If $U_a = 0$ and $U_d = 42$ kJ, find the heat absorbed in the processes *ad* and *db*.

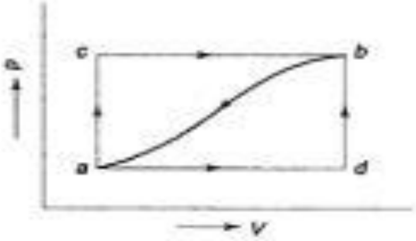


Fig. Ex. 4.2

Solution

$$Q_{acb} = 84 \text{ kJ}$$
$$W_{acb} = 32 \text{ kJ}$$

We have

$$Q_{acb} = U_b - U_a + W_{acb}$$

$\therefore$ $U_b - U_a = 84 - 32 = 52$ kJ *Ans.*

(a) $Q_{adb} = U_b - U_a + W_{adb}$

$= 52 + 10.5$

$= 62.5$ kJ *Ans.*

(b) $Q_{b-a} = U_a - U_b + W_{b-a}$

$= -52 - 21$

$= -73$ kJ *Ans.*

The system liberates 73 kJ of heat.

(c) $W_{adb} = W_{ad} + W_{db} = W_{ad} = 10.5$ kJ

$\therefore$ $Q_{ad} = U_d - U_a + W_{ad}$

$= 42 - 0 + 10.5 = 52.5$ kJ

Now $Q_{adb} = 62.5 \text{ kJ} = Q_{ad} + Q_{db}$

$\therefore$ $Q_{db} = 62.5 - 52.5 = 10$ kJ *Ans.*

Example 4.3 A piston and cylinder machine contains a fluid system which passes through a complete cycle of four processes. During a cycle, the sum of all heat transfers is –170 kJ. The system completes 100 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 (kJ/min)*	*W (kJ/min)*	*ΔE (kJ/min)*
a–b	0	2,170	—
b–c	21,000	0	—
c–d	–2,100	—	–36,600
d–a	—	—	—

Solution Process *a–b*:

$$Q = \Delta E + W$$

$$0 = \Delta E + 2170$$

$$\therefore \quad \Delta E = -2170 \text{ kJ/min}$$

Process *b–c*:

$$Q = \Delta E + W$$

$$21{,}000 = \Delta E + 0$$

$$\therefore \quad \Delta E = 21{,}000 \text{ kJ/min}$$

Process *c–d*:

$$Q = \Delta E + W$$

$$-2100 = -36{,}600 + W$$

$$\therefore \quad W = 34{,}500 \text{ kJ/min}$$

Process *d–a*:

$$\sum_{\text{cycle}} Q = -170 \text{ kJ}$$

The system completes 100 cycles/min.

$$\because \quad Q_{ab} + Q_{bc} + Q_{cd} + Q_{da} = -17{,}000 \text{ kJ/min}$$

$$0 + 21{,}000 - 2{,}100 + Q_{da} = -17{,}000$$

$$\therefore \quad Q_{da} = -35{,}900 \text{ kJ/min}$$

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

$$\therefore \quad \Delta E_{a\text{-}b} + \Delta E_{b\text{-}c} + \Delta E_{c\text{-}d} + \Delta E_{d\text{-}a} = 0$$

$$-2{,}170 + 21{,}000 - 36{,}600 + \Delta E_{d\text{-}a} = 0$$

$$\therefore \quad \Delta E_{d\text{-}a} = 17{,}770 \text{ kJ/min}$$

$$\therefore \quad W_{d\text{-}a} = Q_{d\text{-}a} - \Delta E_{d\text{-}a}$$

$$= -35{,}900 - 17{,}770$$

$$= -53{,}670 \text{ kJ/min}$$

The table becomes

Process	*Q* (kJ/min)	*W* (kJ/min)	Δ*E* (kJ/min)
a–b	0	2,170	– 2,170
b–c	21,000	0	21,000

c–d	– 2,100	34,500	– 36,600
d–a	– 35,900	– 53,670	17,770

Since

Rate of work output $\sum_{\text{cycle}} Q = \sum_{\text{cycle}} W$

$$= -17{,}000 \text{ kJ/min}$$

$$= -283.3 \text{ kW}$$

Ans.

Example 4.4 The internal energy of a certain substance is given by the following equation

$$u = 3.56\, pv + 84$$

where u is given in kJ/kg, p is in kPa, and v is in m^3/kg.

A system composed of 3 kg of this substance expands from an initial pressure of 500 kPa and a volume of 0.22 m^3 to a final pressure 100 kPa in a process in which pressure and volume are related by $pv^{1.2}$ = constant.

(a) If the expansion is quasi-static, find Q, ΔU, and W for the process.

(b) In another process the same system expands according to the same pressure-volume relationship as in part (a), and from the same initial state to the same final state as in part (a), but the heat transfer in this case is 30 kJ. Find the work transfer for this process.

(c) Explain the difference in work transfer in parts (a) and (b).

Solution

(a) $$u = 3.56\, pv + 84$$

$$\Delta u = u_2 - u_1 = 3.56\,(p_2 v_2 - p_1 v_1)$$

∴ $$\Delta U = 3.56\,(p_2 V_2 - p_1 V_1)$$

Now $$p_1 V_1^{\,1.2} = p_2 V_2^{\,1.2}$$

∴ $$V_2 = V_1 \left(\frac{p_1}{p_2}\right)^{1/1.2} = 0.22\left(\frac{5}{1}\right)^{1/1.2}$$

$$= 0.22 \times 3.83 = 0.845 \text{ m}^3$$

∴ $$\Delta U = 356\,(1 \times 0.845 - 5 \times 0.22) \text{ kJ}$$

$$= -356 \times 0.255 = -91 \text{ kJ}$$

Ans. (a)

For a quasi-static process

$$W = \int p\,\mathrm{d}V = \frac{p_2 V_2 - p_1 V_1}{1 - n}$$

$$= \frac{(1 \times 0.845 - 5 \times 0.22)100}{1 - 1.2} = 127.5 \text{ kJ}$$

∴ $$Q = \Delta U + W$$

$$= -91 + 127.5 = 36.5 \text{ kJ}$$

Ans. (a)

(b) Here $Q = 30$ kJ

Since the end states are the same, ΔU would remain the same as in (a).

$$\therefore \quad W = Q - \Delta U$$
$$= 30 - (-91)$$
$$= 121 \text{ kJ}$$

Ans. (b)

(c) The work in (b) is not equal to $\int p\,\mathrm{d}V$ since the process is not quasi-static.