INTRODUCTION

Thermodynamics is the science that deals with heat and work and those properties of substance that bear a relation to heat and work.

Thermodynamics is the study of the patterns of energy change. Most of this course will be concerned with understanding the patterns of energy change.

More specifically, thermodynamics deals with (a) energy conversion and (b) the direction of change.

Basis of thermodynamics is experimental observation. In that sense it is an empirical science. The principles of thermodynamics are summarized in the form of four laws known as zeroth, first, second, and the third laws of thermodynamics.

The zeroth law of thermodynamics deals with thermal equilibrium and provides a means of measuring temperature.

The first law of thermodynamics deals with the conservation of energy and introduces the concept of internal energy.

The second law of thermodynamics dictates the limits on the conversion of heat into work and provides the yard stick to measure the performance of various processes. It also tells whether a particular process is feasible or not and specifies the direction in which a process will proceed. As a consequence it also introduces the concept of entropy.

The third law defines the absolute zero of entropy.

Macroscopic and Microscopic Approaches:

Microscopic approach uses the statistical considerations and probability theory, where we deal with "average" for all particles under consideration. This is the approach used in the disciplines known as kinetic theory and statistical mechanics.

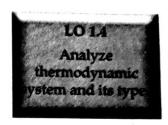
In the macroscopic point of view, of classical thermodynamics, one is concerned with the time-averaged influence of many molecules that can be perceived by the senses and measured by the instruments.

The pressure exerted by a gas is an example of this. It results from the change in momentum of the molecules, as they collide with the wall. Here we are not concerned with the actions of individual molecules but with the time-averaged force on a given area that can be measured by a pressure gage.

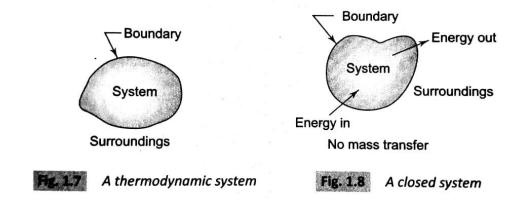
From the macroscopic point of view, we are always concerned with volumes that are very large compared to molecular dimensions, and therefore a system (to be defined next) contains many molecules, and this is called continuum. The concept of continuum loses validity when the mean free path of molecules approaches the order of typical system dimensions

1.7 THERMODYNAMIC SYSTEM AND CONTROL VOLUME

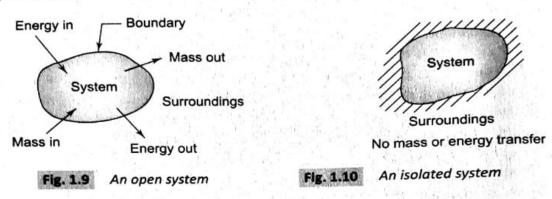
A thermodynamic system is defined as a quantity of matter or a region in space upon which attention is concentrated in the analysis of a problem. Everything external to the system is called the surroundings or the environment. The system is



separated from the surroundings by the system boundary (Fig. 1.7). The boundary may be either fixed or moving. A system and its surroundings together comprise a universe.

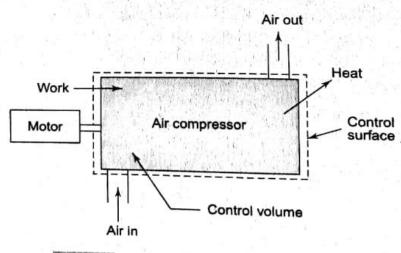


(c) isolated system. The closed system (Fig. 1.8) is a system of fixed mass. There is no mass transfer across the system boundary. There may be energy transfer into or out of the system. A certain quantity of fluid in a cylinder bounded by a piston constitutes a closed system. The open system (Fig. 1.9) is one in which matter crosses the boundary of the system. There may be energy transfer also. Most of the engineering devices are generally open systems, e.g. an air compressor in which air enters at low pressure and leaves at high pressure and there are energy transfers across the system boundary. The isolated system (Fig. 1.10) is one in which there is no interaction between the system and the surroundings. It is of fixed mass and energy, and there is no mass or energy transfer across the system boundary.



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. 1.11), attention is focused 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.



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.

1.8 THERMODYNAMIC PROPERTIES, PROCESSES AND CYCLES

Every system has certain characteristics by which its physical conditions may be described, e.g. volume, temperature, pressure and so on. Such characteristics are called *properties*

of the system. These are all *macroscopic* in nature. When all the properties of a system have definite values, the system is said to exist at a definite *state*. Properties

are the coordinates to describe the state of a system. They are the state variables of the system. Any operation in which one or more of the properties of a system change is called a *change of state*. The succession of states passed through during a change of state is called the *path* of the change of state. When the path is completely specified, the change of state is called a *process*, e.g. a constant pressure process. A thermodynamic cycle is defined as a series of state changes such that the final state is identical with the initial state (Fig. 1.12).

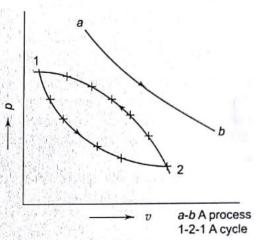


Fig. 1.12 A process and a cycle

Properties may be of two types.

Intensive properties are independent of the mass in the system, e.g. pressure, temperature, and so on. Extensive properties are related to mass, e.g. volume, energy and so on. If mass is increased, the values of the extensive properties also increase. Specific extensive properties, i.e. extensive properties per unit mass, are intensive properties, e.g. specific volume, specific energy and so on.

1.9 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*.

LO 1.6

Elaborate on homogeneous and heterogeneous system

LO 1.5

Explain the concept

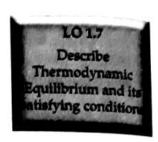
of: State, Property,

Process and Cycle

1.10 THERMODYNAMIC EQUILIBRIUM

A system is said to exist in a state of *thermodynamic* equilibrium when no change in any macroscopic property is registered, if the system is isolated from its surroundings.

An isolated system always reaches in course of time a state of thermodynamic equilibrium and can never depart from it spontaneously.



Therefore, there can be no spontaneous change in any macroscopic property if the system exists in an equilibrium state. Thermodynamics studies mainly the properties of physical systems that are found in equilibrium states.

A system will be in a state of thermodynamic equilibrium, if the conditions for the following three types of equilibrium are satisfied:

- 1. Mechanical equilibrium
- Chemical equilibrium
- Thermal equilibrium

In the absence of any unbalanced force within the system itself and also between the system and the surroundings, the system is said to be in a state of *mechanical equilibrium*. If an unbalanced force exists, either the system alone or both the system and the surroundings will undergo a change of state till mechanical equilibrium is attained.

If there is no chemical reaction or transfer of matter from one part of the system to another, such as diffusion or solution, the system is said to exist in a state of *chemical equilibrium*.

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 non-equilibrium state. If the non-equilibrium 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 non-equilibrium is because of the temperature of the system being different from that of its surroundings, there is a non-uniform 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 and 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 and t_2 . But the intermediate states passed through by the system are non-equilibrium states which cannot be described by thermodynamic coordinates.

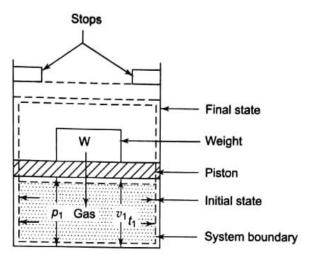
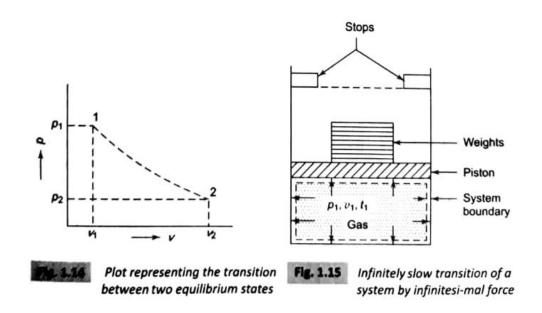


Fig. 1.13 Transition between two equilibrium states by an unbalanced force

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 equilibrium state. Such a process, which is at 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 1-2 (Fig. 1.16) is thus a succession of equilibrium states.

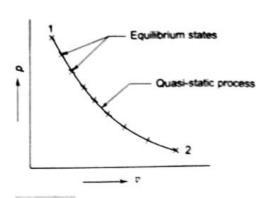


Fig. 1.16 A quasi-static process

If the same slices or very small pieces of weights are now placed slowly one by one on the top of the piston, the piston will move down slowly from state 2 to state 1 by following the same quasi-static path of the succession of equilibrium states (Figs. 1.15 and 1.16). So a quasi-static process is also a reversible process. A reversible process is performed in both ways from 1 to 2 and from 2 to 1 involving infinite time in executing each of the processes.

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 gas and liquid phases in equilibrium.

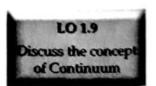
1.12.1 State Postulate

The state of a pure substance of given mass can be fixed by specifying two independent intensive properties, provided the system is in equilibrium. This is known as the 'two-property rule'. The state can thus be represented as a point on thermodynamic property diagrams. Once any two properties of a pure substance are known, other properties can be determined from the available thermodynamic relations.

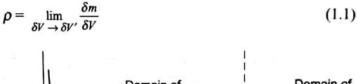
Temperature and specific volume, for example, are always independent properties, and together they can fix the state of a simple compressible system. Temperature and pressure, however, are independent for single-phase systems, but are dependent for two-phase systems.

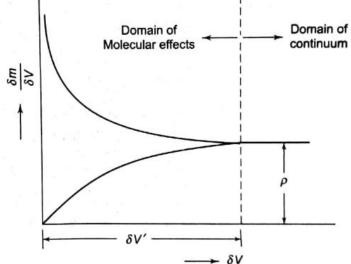
1.13 CONCEPT OF CONTINUUM

From the macroscopic viewpoint, we are always concerned with volumes which are very large compared to molecular dimensions. Even a very small volume of a system is



assumed to contain a large number of molecules so that statistical averaging is meaningful and a property value can be assigned to it. Disregarding the behaviour of individual molecules, matter is here treated as continuous. Let us consider the mass δm in a volume δV surrounding the point P (Fig. 1.17). The ratio $\delta m/\delta V$ is the average mass density of the system within the volume δV . We suppose that at first δV is rather large, and is subsequently shrunk about the point P. If we plot $\delta m/\delta V$ against δV , the average density tends to approach an asymptote as δV increases (Fig. 1.18). However, when δV becomes so small as to contain relatively few molecules, the average density fluctuates substantially with time as molecules pass into and out of the volume in random motion, and so it is impossible to speak of a definite value of $\delta m/\delta V$. The smallest volume which may be regarded as continuous is $\delta V'$. The density ρ of the system at a point is thus defined as





P Φ δm System δV

Fig. 1.17

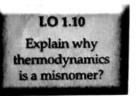
Fig. 1.18 Definition of the macroscopic property, density

Similarly, the fluid velocity at a point P is defined as the instantaneous velocity of the centre of gravity of the smallest continuous volume $\delta V'$.

The concept of continuum loses validity when the mean free path of the molecules approaches the order of magnitude of the dimensions of the vessel, as, for instance, in highly rarefied gases encountered in high vacuum technology, in rocket flights at high altitudes and in electron tubes. In most engineering applications, however, the assumption of a continuum is valid and convenient, and goes hand in hand with the macroscopic point of view.

1.14 THERMOSTATICS

The science of thermodynamics deals with systems existing in thermodynamic equilibrium states which are specified by properties. Infinitely slow quasi-static processes executed by systems are only meaningful in thermodynamic plots.



The name 'thermodynamics' is thus said to be a misnomer, since it does not deal with the dynamics of heat, which is non-quasi-static. The name 'thermostatics' then seems to be more appropriate. However, most of the real processes are dynamic and non-quasi-static, although the initial and final states of the system might be in equilibrium. Such processes can be successfully dealt with by the subject. Hence, the term 'thermodynamics' is not inappropriate.

1.15 UNITS AND DIMENSIONS

In the present text, the SI (System International) system of units has been used. The basic units in this system are given in Table 1.1.



Table 1.1 System: basic units

Quantity	Unit	Symbol
Length (L)	Metre	m
Mass (M)	Kilogram	kg
Time (t)	Second	S
Amount of substance	Mole	mol
Temperature (T)	Kelvin	K
Electric current	Ampere	Α
Luminous intensity	Candela	cd
Plane angle	Radian	rad
Solid angle	Steradian	sr sr

The dimensions of all other quantities are derived from these basic units which are given in Table 1.2.

Table 1.2 SI system: derived units

Quantity	Unit	Symbol	$. \\ Il ternative unit$	In basic units
Force (F)	Newton	N		kg m/s ²
Energy E)	Joule	J J	Nm	$kg m^2/s^2$
Power	Watt	w	J/s	$kg m^2/s^3$
Pressure	Pascal	Pa	. N/m ²	kg/(ms2)
Frequency	Hertz	Hz		s^{-1}
Electric charge	Coulomb	C		As
Electric potential	Volt	V	W/A = J/C	$kg m^2/(s^3 A)$
Capacitance	Farad	F	C/V	$s^4 A^2/(kg m^2)$
	Ohm	Ω	V/A	$kg m^2/(s^3 A^2)$
	Weber	Wb	Vs	$kg m^2/(s^2 A)$
	Tesla	T	Wb/m ²	$kg/(s^2 A)$
# 1970 MET C 50 C 100 E 50 PROBLEM C C C C C C C C C C C C C C C C C C C	Henry	н	Wb/A	$kg m^2/(s^2 A^2)$
Electrical resistance Magnetic flux Magnetic flux density Inductance	Ohm Weber Tesla	Ω Wb T	V/A Vs Wb/m ²	kg m ² /(s ² kg m ² /(s ² kg/(s ² A)

It is often convenient and desirable to use multiples of various units, the standard list of which is given in Table 1.3.

Lacted	Profe	Linter	Prefi
1012	tera, T	10-3	milli, m
109	giga, G	10-6	micro, μ
106	mega, M	10-9	nano, n
103	kilo, k	10-12	pico, p

Table 1.3 SI system: standard multipliers

1.15.1 Force

The force acting on a body is defined by Newton's second law of motion. The unit of force is the newton (N). A force of one newton produces an acceleration of 1 ms⁻² when applied to a mass of 1 kg.

$$1 N = 1 kg m/s^2$$

The weight of a body (W) is the force with which the body is attracted to the centre of the earth. It is the product of its mass (m) and the local gravitational acceleration (g), i.e.

$$W = mg$$

The value of g at sea level is 9.80665 m/s². The mass of a substance remains constant with elevation, but its weight varies with elevation.

1.15.2 Pressure

Pressure is the normal force exerted by a system against unit area of the bounding surface. If δA is a small area and $\delta A'$ is the smallest area from continuum consideration, and δF_n is the component of force normal to δA (Fig. 1.19), the pressure p at a point on the wall is defined as



$$p = \lim_{\delta A \to \delta A'} \frac{\delta F_n}{\delta A}$$

The pressure p at a point in a fluid in equilibrium is the same in all directions.

The unit for pressure in the SI system is pascal (Pa), which is the force of one newton acting on an area of 1 m².

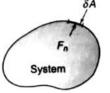


Fig. 1.19 Definition of pressure

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

The unit of pascal is very small. Very often kilo-pascal (kPa) or mega-pascal (MPa) is used.

Two other units, not within the SI system of units, continue to be widely used. These are the bar, where

$$1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa} = 0.1 \text{ MPa}$$

and the standard atmosphere, where

One bar is thus close to 1 atm.

Most instruments indicate pressure relative to the atmospheric pressure, whereas the pressure of a system is its pressure above zero, or relative to a perfect vacuum (Fig. 1.20). The pressure relative to the atmosphere is called *gauge pressure*. The pressure relative to a perfect vacuum is called *absolute pressure*.

Absolute pressure = Gauge pressure + Atmospheric pressure

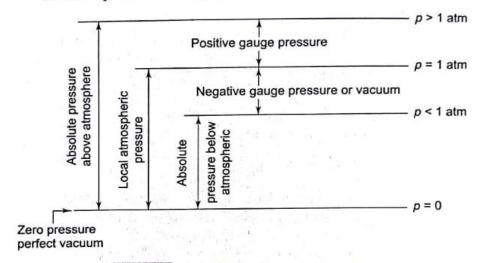


Fig. 1.20 Relationship between pressures

When the pressure in a system is less than the atmospheric pressure, the gauge pressure becomes negative, but is frequently designated by a positive number and is called *vacuum*. For example, 16 cm Hg vacuum will be

$$\frac{76-16}{76} \times 1.013 = 0.80 \text{ atm}$$

$$p_{\text{abs}} = p_{\text{atm}} - p_{\text{vac}}$$

Figure 1.21 shows a few pressure measuring devices. Figure 1.21(a) shows the Bourdon gauge which measures the difference between the system pressure inside the tube and atmospheric pressure. It relies on the deformation of a bent hollow tube of suitable material which, when subjected to the pressure to be measured on the inside (and atmospheric pressure on the outside), tends to unbend. This moves a pointer through a suitable gear-and lever mechanism against a calibrated scale. Figure 1.21(b) shows an open U-tube indicating gauge pressure, and Fig. 1.21(c) shows an open U-tube indicating vacuum. Figure 1.21(d) shows a closed U-tube indicating absolute pressure. If p is atmospheric pressure, this is a barometer. These are called U-tube manometers.

Thus,

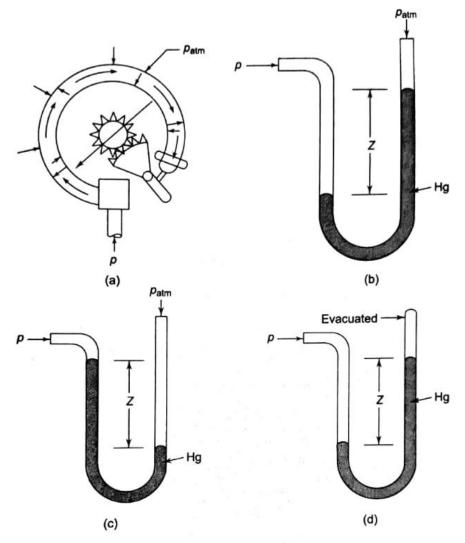


Fig. 1.21 Pressure gauges: (a) Bourdon gauge, (b) Open U-tube indicating gauge pressure, (c) Open U-tube indicating vacuum, (d) Closed U-tube indicating absolute pressure

If Z is the difference in the heights of the fluid columns in the two limbs of the U-tube [Figs. 1.21(b) and (c)], ρ is the density of the fluid and g is the acceleration due to gravity, then from the elementary principle of hydrostatics, the gauge pressure p_g is given by

 $p_g = Z\rho g \left[m \cdot \frac{kg}{m^3} \frac{m}{s^2} \right] = Z\rho g N/m^2$

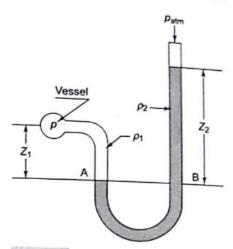
If the fluid is mercury having $\rho = 13,616 \text{ kg/m}^3$, one metre head of mercury column is equivalent to a pressure of 1.3366 bar, as shown below.

1 m Hg =
$$Z\rho g$$
 = 1 × 13616 × 9.81
= 1.3366 × 10⁵ N/m² = 1.3366 bar

The manometer is a sensitive, accurate and simple device, but it is limited to fairly small pressure differentials and, because of the inertia and friction of the liquid, is not suitable for fluctuating pressures,

unless the rate of pressure change is small. A diaphragm-type pressure transducer along with a cathode ray oscilloscope can be used to measure rapidly fluctuating pressures. The unit of 1 mm Hg pressure is called *torr*, so that

Figure 1.22 shows a typical U-tube manometer, one end of which is connected to the vessel the pressure of which is to be measured and the other end is open to atmosphere exerting pressure $p_{\rm atm}$. The manometric fluid may be mercury, water, alcohol, oil and so on. The pressure along the horizontal line AB is the same in both the limbs of the manometer, so that



....mmmmmmmm

Fig. 1.22 Pressure measurement by a manometer

$$p + \rho_1 gZ_1 = p_{atm} + \rho_2 gZ_2$$

If the vessel contains a gas of density ρ_1 and since the density of the manometric fluid (say Hg), $\rho_2 >> \rho_1$,

$$p - p_{\text{atm}} = \rho_2 g Z_2 = p_{\text{gauge}}$$

1.15.3 Specific Volume and Density

Volume (V) is the space occupied by a substance and is measured in m^3 . The specific volume (V) of a substance is defined as the volume per unit mass and is measured in m^3/kg . From continuum consideration the specific volume at a point is defined as

$$v = \lim_{\delta V \to \delta V'} \frac{\delta V}{\delta m}$$

where dV' is the smallest volume for which the system can be considered a continuum. Density (ρ) is the mass per unit volume of a substance, which has been discussed earlier, and is given in kg/m^3 .

$$\rho = \frac{m}{n}$$

In addition to m³, another commonly used unit of volume is the litre (1).

$$1 l = 10^{-3} \text{ m}^3$$

The specific volume or density may be given either on the basis of mass or in respect of mole. A *mole* of a substance has a mass numerically equally to the molecular weight of the substance. One gram mol of oxygen has a mass of 32 g and 1 kg mol (or kmol) of nitrogen has a mass of 28 kg. The symbol \bar{v} is used for molar specific volume (m³/kmol).

1.15.4 Energy

Energy is the capacity to exert a force through a distance, and manifests itself in various forms. Engineering processes involve the conversion of energy from one form to another, the transfer of energy from place to place and the storage of energy in various forms, utilising a working substance.

The unit of energy in the SI system is Nm or J (joule). The energy per unit mass is the specific energy, the unit of which is J/kg.

1.15.5 Power

The rate of energy transfer or storage is called power. The unit of power is watt (W), kilowatt (kW) or megawatt (MW).

$$1 W = 1 J/s = 1 Nm/s$$

 $1 kW = 1000 W$

SOLVED EXAMPLES

Example 1.1 The pressure of gas in a pipeline is measured with a mercury manometer having one limb open to the atmosphere (Fig. 1.23). If the difference in the height of mercury in the two limbs is 562 mm, calculate the gas pressure. The barometer reads 761 mm Hg, the acceleration due to gravity is 9.79 m/s², and the density of mercury is 13,640 kg/m³. [LO 1.12]

Solution At plane AB, we have

$$p = p_0 + \rho g z$$

Now

$$p_0 = \rho g z_0$$

where z_0 is the barometric height, ρ the density of mercury and p_0 the atmospheric pressure.

Therefore.

$$p = \rho g (z + z_0)$$

= 13,640 kg/m³ × 9.79 m/s² (0.562 + 0.761) m
= 177 × 10³ N/m² = 177 kPa = 1.77 bar = 1.746 atm

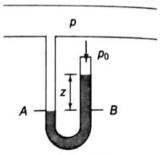


Fig. 1.23

Example 1.2 A turbine is supplied with steam at a gauge pressure of 1.4 MPa. After expansion in the turbine the steam flows into a condenser which is maintained at a vacuum of 710 mmHg. The barometric pressure is 772 mmHg. Express the inlet and exhaust steam pressures in pascals (absolute). Take the density of mercury as 13.6×10^3 kg/m³. [LO 1.12]

Solution The atmospheric pressure p_0

$$= \rho g z_0 = 13.6 \times 10^3 \text{ kg/m}^3 \times 9.81 \text{ m/s}^2 \times 0.772 \text{ m}$$
$$= 1.03 \times 10^5 \text{ Pa}$$

Inlet steam pressure

=
$$[(1.4 \times 10^6) + (1.03 \times 10^5)]$$
 Pa
= 15.03×10^5 Pa = 1.503 MPa

Condenser pressure

=
$$(0.772 - 0.710)$$
 m × 9.81 m/s² × 13.6 × 10³ kg/m³
= 0.827×10^4 Pa = **8.27 kPa**

- Example 1.3 Convert the following readings of pressure to kPa, assuming that the barometer reads 760 mm of Hg. [LO 1.12]
 - (a) 40 cmHg vacuum
 - (b) 90 cmHg gauge
 - (c) 1.2 m of H D gauge

Levels of Difficulty

- Low complexity: Level 1 and Level 2 Category
- Medium complexity: Level 3 and Level 4 Category
- High complexity: Level 5 and Level 6 Category

Solution

(a)
$$p_{\text{vacuum}} = h\rho g = (40 \times 10^{-2}) \times (13.6 \times 10^{3}) \times 9.8$$

$$= 53.31 \times 10^{3} \text{ N/m}^{2} = 53.31 \text{ kPa}$$

$$p_{\text{absolute}} = p_{\text{atm}} - p_{\text{vac}}$$

$$= (760 - 400) \times 9.8 \times 13.6 \times 10^{3}$$

$$= 48 \times 10^{3} \text{ N/m}^{2} = 48 \text{ kPa}$$
Also,
$$p_{\text{abs}} = 101.325 - 53.31 = 48.015 \text{ kPa}$$
(b)
$$p_{\text{gauge}} = h \rho g$$

$$= (90 \times 10^{-2}) \times (13.6 \times 10^{3}) \times 9.8$$

$$= 120 \times 10^{3} \text{ N/m}^{2} = 120 \text{ kPa}$$
Since
$$p_{\text{atm}} = 760 \text{ mm Hg} = 101.325 \text{ kPa}$$

$$p_{\text{abs}} = p_{\text{gauge}} + p_{\text{atm}}$$

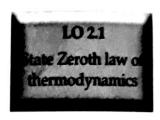
$$= 120 + 101.325 = 221.325 \text{ kPa}$$
(c)
$$p_{\text{gauge}} = h \rho g = 1.2 \text{ m} \times 1000 \frac{\text{kg}}{\text{m}^{3}} \times 9.81 \frac{\text{m}}{\text{s}^{2}}$$

$$= 11.772 \text{ kPa}$$

$$p_{\text{abs}} = 11.772 + 101.325 = 113.097 \text{ kPa}$$

2.1 ZEROTH LAW OF THERMODYNAMICS

The property which distinguishes thermodynamics from other sciences is temperature. One might say that temperature bears as important a relation to thermodynamics as force does to statics or velocity does to dynamics. Temperature



is associated with the ability to distinguish hot from cold. When two bodies at different temperatures are brought into contact, after sometime they attain a common temperature and are then said to exist in thermal equilibrium.

When a body A is in thermal equilibrium with a body B, and also separately with a body C, then bodies B and C will be in thermal equilibrium with each other.

This is known as the zeroth law of thermodynamics. It is the basis of temperature measurement.

In order to obtain a quantitative measure of temperature, a reference body is used, and a certain physical characteristic of this body which changes with temperature is selected. The changes in the selected characteristic may be taken as an indication

of changes in temperature. The selected characteristic is called the *thermometric* property, and the reference body which is used in the determination of temperature is called the *thermometer*. A very common thermometer consists of a small amount of mercury in an evacuated capillary tube. In this case the extension of the mercury in the tube is used as the thermometric property.

There are five different kinds of thermometer, each with its own thermometric property, as shown in Table 2.1.

2.2 MEASUREMENT OF TEMPERATURE—THE REFERENCE POINTS

The temperature of a system is a property that determines whether or not a system is in thermal equilibrium with other systems. If a body is at, say, 70° C, it will be 70° C, whether measured by a mercury-in-glass thermometer, resistance thermometer or constant volume gas thermometer. If X is the thermometric property, let us arbitrarily choose for the temperature common to the thermometer and to all systems in thermal equilibrium with it the following linear function of X:



Table 2.1 Thermometers and thermometric properties

Thermometer	Thermometric property	Symbol
1. Constant volume gas thermometer	Pressure	p
2. Constant pressure gas thermometer	Volume	V
3. Electrical resistance thermometer	Resistance	R
4. Thermocouple	Thermal e.m.f.	ε
5. Mercury-in-glass thermometer	Length	L

 $\theta(X) = aX$, where a is an arbitrary constant.

If X_1 corresponds to $\theta(X_1)$, then X_2 will correspond to

$$\frac{\theta(X_1)}{X_1} \cdot X_2$$

$$\theta(X_2) = \frac{\theta(X_1)}{X_1} \cdot X_2$$
(2.1)

that is

Two temperatures on the linear X scale are to each other as the ratio of the corresponding X's.

2.2.1 Method Used Before 1954

The thermometer is first placed in contact with the system whose temperature $\theta(X)$ is to be measured, and then in contact with an arbitrarily chosen standard system in an easily reproducible state where the temperature is $\theta(X_1)$. Thus,

$$\frac{\theta(X_1)}{\theta(X)} = \frac{X_1}{X} \tag{2.2}$$

Then the thermometer at the temperature $\theta(X)$ is placed in contact with another arbitrarily chosen standard system in another easily reproducible state where the temperature is $\theta(X_2)$. It gives

$$\frac{\theta(X_2)}{\theta(X)} = \frac{X_2}{X} \tag{2.3}$$

From Eqs. (2.2) and (2.3)

$$\frac{\theta(X_1) - \theta(X_2)}{\theta(X)} = \frac{X_1 - X_2}{X}$$
or,
$$\theta(X) = \frac{\theta(X_1) - \theta(X_2)}{X_1 - X_2} \cdot X$$
(2.4)

If we assign an arbitrary number of degrees to the temperature interval $\theta(X_1) - \theta(X_2)$, then $\theta(X)$ can be calculated from the measurements of X, X_1 and X_2 .

An easily reproducible state of an arbitrarily chosen standard system is called a fixed point. Before 1954, there were two fixed points: (i) the ice point, the temperature at which pure ice co-existed in equilibrium with air-saturated water at one atmosphere pressure, and (ii) the steam point, the temperature of equilibrium between pure water and pure steam at one atmosphere pressure. The temperature interval, $\theta(X_1) - \theta(X_2)$, between these two fixed points was chosen to be 100 degrees.

The use of two fixed points was found unsatisfactory and later abandoned, because of (i) the difficulty of achieving equilibrium stage/pt. between pure ice and air-saturated water (since when ice melts, it surrounds itself only with pure water and prevents intimate contact with air-saturated water), and (ii) extreme sensitiveness of the steam point to the change in pressure.

2.2.2 Method in Use After 1954

Since 1954 only one fixed point has been in use, viz. the triple point of water, the state at which ice, liquid water and water vapour co-exist in equilibrium. The temperature at which this state exists is arbitrarily assigned the value of 273.16 degrees Kelvin, or 273.16 K (the reason for using Kelvin's name will be explained later). Designating the triple point of water by θ_t , and with X_t being the value of the thermometric property when the body, whose temperature θ is to be measured, is placed in contact with water at its triple point, it follows that

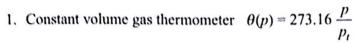
$$\theta_{t} = aX_{t}$$

$$a = \frac{\theta_{t}}{X_{t}} = \frac{273.16}{X_{t}}$$
Therefore,
$$\theta = aX = \frac{273.16}{X_{t}} \cdot X$$
or,
$$\theta = 273.16 \frac{X}{X_{t}}$$
(2.5)

The temperature of the triple point of water, which is an easily reproducible state, is now the standard fixed point of thermometry.

COMPARISON OF THERMOMETERS 2.3

Applying the above principle to the five thermometers listed in Table 2.1, the temperatures are given as follows:



2. Constant pressure gas thermometer
$$\theta(V) = 273.16 \frac{V}{V_t}$$

3. Electric resistance thermometer
$$\theta(R) = 273.16 \frac{R}{R_t}$$

4. Thermocouple
$$\theta(\varepsilon) = 273.16 \frac{\varepsilon}{\varepsilon_t}$$
5. Liquid-in-glass thermometer
$$\theta(L) = 273.16 \frac{L}{L_t}$$

5. Liquid-in-glass thermometer
$$\theta(L) = 273.16 \frac{L}{L}$$

LO 2.3 Compare standard parameters of various thermometers

If the temperature of a given system is a measured simultaneously with each of the five thermometers, it is a found that there is a considerable difference among the readings. The smallest variation is, however, observed among different gas thermometers. That is why a gas is chosen as the standard thermometric substance.

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:

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

where \bar{R} is the universal gas constant, 8.3143 J/mol K and \overline{v} is the molar specific volume, m³/gmol. (see Sec. 10.3.). Dividing Eq. (2.6) by the molecular weight μ ,

LO 2.4

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

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

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

$$PV = mRT$$
(2.8)

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,

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \tag{2.9}$$

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 the lip L of the capillary. The pressure in the bulb is used as a thermometric property and is given by

$$p = p_0 + \rho_{\rm M} Zg$$

where p_0 is the atmospheric pressure, $\rho_{\rm M}$ is the density of mercury.

When the bulb is brought in contact with the system whose temperature is to be measured, the

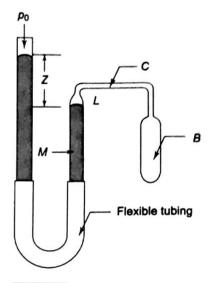


Fig. 2.1 Constant volume gas thermometer

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,

$$\Delta T = \frac{V}{R} \Delta p \tag{2.10}$$

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

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.

$$\Delta T = \frac{p}{R} \Delta V \tag{2.11}$$

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 is 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_i is 1000 mm Hg. Keeping the volume V constant, let the following procedure be conducted:



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

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

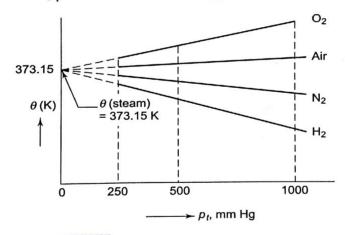
2. Remove some gas from the bulb so that when it is surrounded by water at its triple point, the pressure p_t is 500 mm Hg. Determine the new value of p and then θ for steam condensing at 1 atm.

$$\theta = 273.16 \frac{p}{500}$$

- 3. Continue reducing the amount of gas in the bulb so that p_i and p have smaller and smaller values, e.g. p, having, say, 250 mm Hg, 100 mm Hg and so on. At each value of p_t calculate the corresponding θ .
- 4. Plot θ vs. p_t and extrapolate the curve to the axis where $p_t = 0$. Read from the graph

$$\lim_{p_t\to 0}\theta$$

The graph, as shown in Fig. 2.2, indicates that although the readings of a constant volume gas thermometer depend upon the nature of the gas, all gases indicate the same temperature as p, is lowered and made to approach zero.



Ideal gas temperature for steam point Fig. 2.2

A similar series of tests may be conducted with a constant pressure gas thermometer. The constant pressure may first be taken to be 1000 mm Hg, then 500 mm Hg, etc. and at each value of p, the volumes of gas V and V_t may be recorded when the bulb is surrounded by steam condensing at 1 atm and the triple point of water, respectively. The corresponding value of heta may be calculated from

$$\theta = 273.16 \ \frac{V}{V_t}$$

and θ vs. p may be plotted, similar to Fig. 2.2. It is found from the experiments that all gases indicate the same value of θ as p approaches zero.

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

LO 3.1

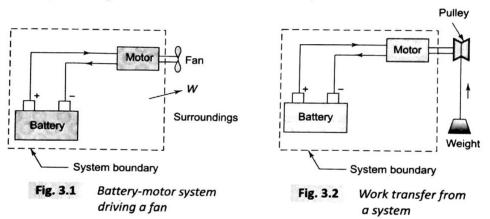
Define work transfer in thermodynamics and discuss its sign convention

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.



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.

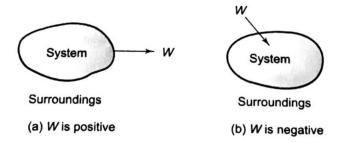


Fig. 3.3 Work interaction between a system and the surroundings

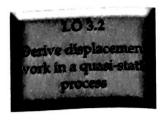
The unit of work is N.m or Joule [1 Nm = 1 Joule]. The rate at which work is done by, or upon, the system is known as *power*. The unit of power is J/s or watt.

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 and V_1 . The piston is the only boundary which moves due

 p_1 and V_1 . The piston is the only country 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 be 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 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



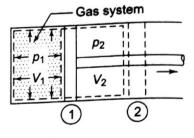


Fig. 3.4 pdV work

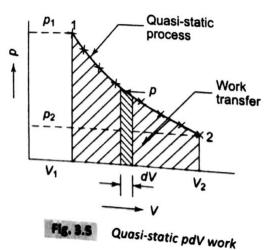
$$dW = F \cdot dl = padl = pdV \tag{3.1}$$

where dV = adl = infinitesimal displacement volume. The differential sign in δW 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

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

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.



25

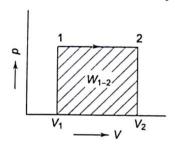
3.2.1 pdV-Work in Various Quasi-Static Processes

1. Constant pressure process (Fig. 3.6) (isobaric or isopiestic process)

$$W_{1-2} = \int_{V_1}^{V_2} p dV = p(V_2 - V_1)$$
 (3.2)

2. Constant volume process (Fig. 3.7) (isochoric process)

$$W_{1-2} = \int p dV = 0 {3.3}$$



 $\begin{array}{c|c}
p_1 & & & \\
\uparrow & & & \\
p_2 & & & \\
\end{array}$

Fig. 3.6 Constant pressure process

Fig. 3.7 Constant volume process

3. Process in which pV = C (Fig. 3.8) (isothermal process)

$$W_{1-2} = \int_{V_1}^{V_2} p dV \qquad pV = p_1 V_1 = C$$

$$p = \frac{(p_1 V_1)}{V}$$

$$W_{1-2} = p_1 V_1 \int_{V_1}^{V_2} \frac{dV}{V} = p_1 V_1 \ln \frac{V_2}{V_1}$$

$$= p_1 V_1 \ln \frac{p_1}{p_2}$$
(3.4)

4. Process in which $pV^n = C$, where n is a constant (Fig. 3.9) (polytropic process).

$$pV^{n} = p_{1} V_{1}^{n} = p_{2} V_{2}^{n} = C$$

$$\Rightarrow \frac{\left(p_{1}V_{1}^{n}\right)}{V^{n}}$$

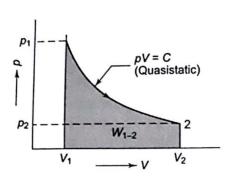
$$\Rightarrow W_{1-2} = \int_{V_{1}}^{V_{2}} p dV = \int_{V_{1}}^{V_{2}} \frac{p_{1}V_{1}^{n}}{V^{n}} \cdot dV = \left(p_{1} V_{1}^{n}\right) \left[\frac{V^{-n+1}}{-n+1}\right]_{V_{1}}^{V_{2}}$$

$$= \frac{p_{1}V_{1}^{n}}{1-n} \left(V_{2}^{1-n} - V_{1}^{1-n}\right) = \frac{p_{2}V_{2}^{n} \times V_{2}^{1-n} - p_{1}V_{1}^{n} \times V_{1}^{1-n}}{1-n}$$

$$= \frac{p_{1}V_{1} - p_{2}V_{2}}{n-1} = \frac{p_{1}V_{1}}{n-1} \left[1 - \left(\frac{p_{2}}{p_{1}}\right)^{\frac{n-1}{n}}\right]$$
(3.5)

Similarly, for process in which $pv^{\gamma} = c$, where $\gamma = c_p/c_v$,

$$W_{1-2} = \frac{p_1 V_1}{n-1} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{\gamma - 1}{\gamma}} \right]$$
 (3.5a)



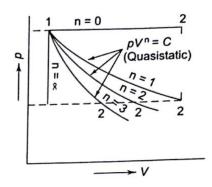


Fig. 3.8 Process in which pV = Constant

Fig. 3.9 Proces

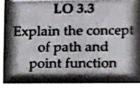
Process in which $pV^n = Constant$

3.3 PATH FUNCTION AND POINT FUNCTION

With reference to Fig. 3.10, 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 implied.



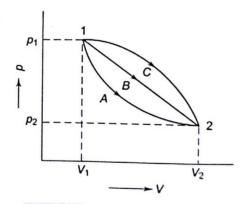


Fig. 3.10 Work—A path function

$$\int_{V_1}^{V_2} dV = V_2 - V_1$$

The change in volume thus depends only on the end states of the system irrespective of the path the system follows. realized

On the other hand, work done in a quasi-static process between two given states depends on the path followed.

Rather,
$$\int_1^2 dW \neq W_2 - W_1$$

$$\int_1^2 dW = W_{1-2} \quad \text{or} \quad _1 W_2$$

To distinguish an inexact differential dW from an exact differential dV or dp the differential sign is being cut by a line at its top.

Fom Eq. (3.1),
$$dV = \frac{1}{p} d^{2}W$$
 (3.6)

Here, 1/p is called the *integrating factor*. Therefore, an inexact differential δW when multiplied by an integrating factor 1/p becomes an exact differential dV.

For a cyclic process, the initial and final states of the system are the same, and hence, the change in an property is zero, i.e.

$$\oint dV = 0, \ \oint dp = 0, \ \oint dT = 0$$
(3.7)

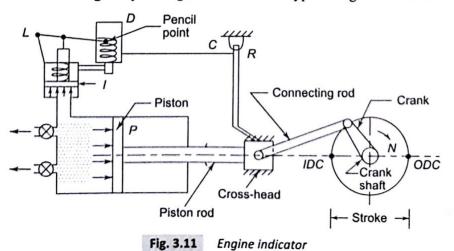
where the symbol \oint denotes the cyclic integral for the closed path. Therefore, the cyclic integral of a property is always zero.

3.4 INDICATOR DIAGRAM

A reciprocating engine (Figs. 1.2 and 13.4) where the reciprocating motion of the piston is converted to the rotary motion of the crank shaft can be (i) single-acting or double-acting, depending on whether the working fluid does work either on one side or both

LO 3.4
Calculate the work
done in an engine
cycle using indicator
diagram

sides of the piston, (ii) two-stroke or four-stroke, depending on whether the engine cycle is completed by two or four strokes of the piston, and (iii) Single cylinder or multi-cylinder, depending on the number of cylinders in the engine. An indicator diagram is a trace made by a recording pressure gauge, called the indicator, attached to the cylinder of a reciprocating engine. This represents the work done in one engine cycle. Figure 3.11 shows a typical engine indicator.



3.6 FREE EXPANSION WITH ZERO WORK TRANSFER

Work transfer is identified only at the boundaries of a system. It is a boundary phenomenon, and a form of energy in transit crossing the boundary. Let us consider a gas separated from the vacuum by a partition (Fig. 3.17). Let the partition be



removed. The gas rushes to fill the entire volume. The expansion of a gas against vacuum is called *free expansion*. If we neglect the work associated with the removal of partition, and consider the gas and vacuum together as our system (Fig. 3.17a), there is no work transfer involved here, since no work crosses the system boundary, and hence

$$\int_{1}^{2} dW = 0, \quad \text{although } \int_{1}^{2} p dV \neq 0$$

If only the gas is taken as the system (Fig. 3.17b), when the partition is removed there is a change in the volume of the gas, and one is tempted to calculate the work from the expression $\int_{1}^{2} p dV$. However, this is not a quasi-static process, although the initial

and final end states are in equilibrium. Therefore, the work cannot be calculated from this relation. The two end states can be located on the p-V diagram and these are joined by a dotted line (Fig. 3.17c) to indicate that the process had occurred. However, if the vacuum space is divided into a large number of small volumes by partitions and the partitions are removed one by one slowly (Fig. 3.17d), then every state passed through by the system is an equilibrium state and the work done can then be estimated from

the relation $\int_{1}^{2} p dV$ (Fig. 3.17e). Yet, in free expansion of a gas, there is no resistance to the fluid at the system boundary as the volume of the gas increases to fill up the

vacuum space. Work is done by a system to overcome some resistance. Since vacuum does not offer any resistance, there is no work transfer involved in free expansion.

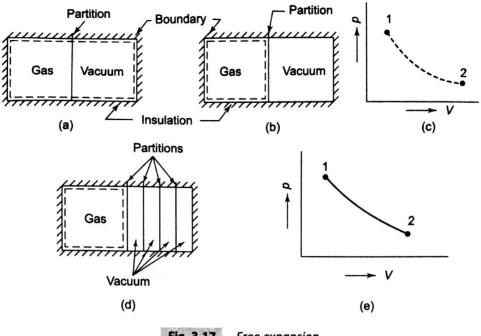


Fig. 3.17 Free expansion

3.7 NET WORK DONE BY A SYSTEM

Often different forms of work transfer occur simultaneously during a process executed by a system. When all these work interactions have been evaluated, the total or net work done by the system would be equal to the algebraic sum of these as given below:

$$W_{\text{total}} = W_{\text{displacement}} + W_{\text{shear}} + W_{\text{electrical}} + W_{\text{stirring}} + \dots$$

3.8 HEAT TRANSFER

If a system has a non-adiabatic boundary, its temperature is not independent of the temperature of the surroundings, and for the system between the states 1 and 2, the work W depends on the path, and the differential dW is inexact.



The work depends on the terminal states 1 and 2 as well as the non-adiabatic path connecting them. For consistency with the principle of conservation of energy, some other type of energy transfer besides work must have taken place between the system and surroundings. This type of energy transfer must have occurred because of the temperature difference between the system and its surroundings, and it is identified as 'heat'. Thus, when an effect in a system occurs solely as a result of temperature difference between the system and some other system, the process in which the effect occurs shall be called a transfer of heat from the system at the higher temperature to the system at the lower temperature.

Heat is defined as the form of energy that is transferred across a boundary by virtue of a temperature difference. The temperature difference is the 'potential' or 'force' and heat transfer is the 'flux'.

The transfer of heat between two bodies in direct contact is called *conduction*. Heat may be transferred between two bodies separated by empty space or gases by the mechanism of *radiation* through electromagnetic waves. A third method of heat transfer is *convection* which refers to the transfer of heat between a wall and a fluid system in motion.

The direction of heat transfer is taken from the high temperature system to the low temperature system. Heat flow into a system is taken to be positive, and heat flow out of a system is taken as negative (Fig. 3.18). The symbol Q is used for heat transfer, i.e. the quantity of heat transferred within a certain time.

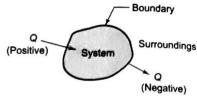


Fig. 3.18 Direction of heat transfer

Heat is a form of energy in transit (like work transfer). It is a boundary phenomenon, since it occurs only at the boundary of a system. Energy transfer by virtue of temperature difference only is called *heat transfer*. All other energy interactions may be termed as work transfer.

Heat is not that which inevitably causes a temperature rise. When heat is transferred to an ice-and-water mixture, the temperature does not rise until all the ice has melted. When a temperature rise in a system occurs, it may not be due to heat transfer, since a temperature rise may be caused by work transfer also. Heat, like work, is not a conserved quantity, and is not a property of a system.

A process in which no heat crosses the boundary of the system is called an adiabatic process.

Thus, an adiabatic process is one in which there is only work interaction between the system and its surroundings.

A wall which is impermeable to the flow of heat is an adiabatic wall, whereas a wall which permits the flow of heat is a diathermic wall.

The unit of heat is Joule in S.I. units.

The rate of heat transfer or work transfer is given in kW or W.

3.9 HEAT TRANSFER—A PATH FUNCTION

The heat flow Q in a process can be quantified in terms of the work W done in the same process between two given terminal states. Work W is different for different non-adiabatic processes between these two states and it is not conserved. However, from the principle of conservation of



energy, the difference (Q - W) is conserved for all paths between the same two states. The heat flow Q, like W, depends on the process and is path-dependent and not a property.

Heat transfer is a path function, that is, the amount of heat transferred when a system changes from state 1 to state 2 depends on the intermediate states through we write

Heat transfer is a path function, that is, the amount of heat transferred when a which the system passes, i.e. its path. Therefore, dQ is an inexact differential and

$$\int_{1}^{2} dQ = Q_{1-2} \quad \text{or} \quad {}_{1}Q_{2}$$

The displacement work is given by

$$W_{1-2} = \int_{1}^{2} dW = \int_{1}^{2} p dV$$

It is valid for a quasi-static process, and the work transfer involved is represented by the area under the path on p-v diagram (Fig. 3.19a). Whenever there is a difference in pressure, there will be displacement work. The pressure difference is the cause and work transfer is the effect. The work transfer is equal to the integral of the product of the intensive property, p and the differential change in the extensive property, dV.

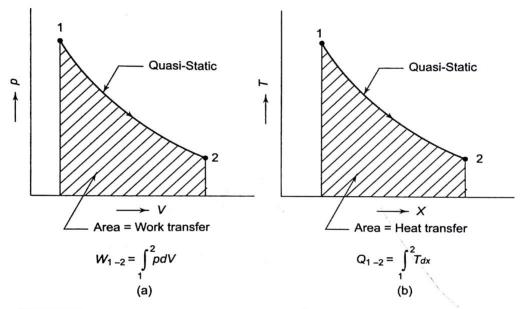


Fig. 3.19 Representation of work transfer and heat transfer in quasi-static processes on p-v and T-x coordinates

Likewise, whenever there is a difference in temperature, there will be heat flow. The temperature difference is the cause and heat transfer is the effect. Just like the displacement work, the heat transfer can also be written as the integral of the product of the intensive property T and the differential change of an extensive property, say X (Fig. 3.19b).

$$Q_{1-2} = \int_{1}^{2} dQ = \int_{1}^{2} T dX \tag{3.26}$$

It must also be valid for a quasi-static process only, and the heat transfer involved is represented by the area under the path 1-2 in T-X plot (Fig. 3.19b). Heat transfer is, therefore, a path function, i.e. the amount of heat transferred when a system changes from state 1 to state 2 depends on the path the system follows (Fig. 3.19b). Therefore dQ is an inexact differential. Now,

$$dQ = T dX$$

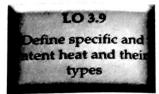
where X is an extensive property and dX is an exact differential.

$$dX = \frac{1}{T}dQ ag{3.27}$$

To make δQ integrable, i.e., an exact differential, it must be multiplied by an integrating factor which is, in this case, 1/T. The extensive property X is yet to be defined. It has been introduced in Chapter 7 and is called 'entropy'.

3.10 SPECIFIC HEAT AND LATENT HEAT

The *specific heat* of a substance is defined as the amount of heat required to raise a unit mass of the substance through a unit rise in temperature. The symbol c will be used for specific heat.



$$c = \frac{Q}{m \cdot \Delta t} \text{ J/kg K}$$

where Q is the amount of heat transfer (J), m is, the mass of the substance (kg) and Δt , the rise in temperature (K).

Since heat is not a property, as explained later, so the specific heat is qualified with the process through which exchange of heat is made. For gases, if the process is at constant pressure, it is c_p , and if the process is at constant volume, it is c_v . For solids and liquids, however, the specific heat does not depend on the process. An elegant manner of defining specific heats, c_v and c_p , in terms of properties is given in Sections 4.5 and 4.6.

The product of mass and specific heat (mc) is called the *heat capacity* of the substance. The capital letter C, C_p or C_v is used for heat capacity.

The latent heat is the amount of heat transfer required to cause a phase change in unit mass of a substance at a constant pressure and temperature. There are three phases in which matter can exist: solid, liquid and vapour or gas. The latent heat of fusion $(l_{\rm fu})$ is the amount of heat transferred to melt unit mass of solid into liquid, or to freeze unit mass of liquid into solid. The latent heat of vaporisation $(l_{\rm vap})$ is the quantity of heat required to vaporise unit mass of liquid into vapour or condense unit mass of vapour into liquid. The latent heat of sublimation $(l_{\rm sub})$ is the amount of heat transferred to convert unit mass of solid to vapour or vice versa. $l_{\rm fu}$ is not much affected by pressure, whereas $l_{\rm vap}$ is highly sensitive to pressure.

3.11 POINTS TO REMEMBER REGARDING HEAT TRANSFER AND WORK TRANSFER

- Heat transfer and work transfer are the energy interactions. A closed system
 and its surroundings can interact in two ways: by heat transfer and by work
 transfer. Thermodynamics studies how these interactions bring about property
 changes in a system.
- The same effect in a closed system can be brought about either by heat transfer or by work transfer. Whether heat transfer or work transfer has taken place or

SOLVED EXAMPLES

Example 3.1 An object of 40 kg mass falls freely under the influence of gravity from an elevation of 100 m above the earth's surface. The initial velocity is directed downward with a magnitude of 100 m/s. Ignoring the effect of air resistance, what is the magnitude of the velocity, in m/s, of the object just before it strikes the earth? The acceleration of gravity is $g = 9.81 \text{ m/s}^2$. [LO 3.2]

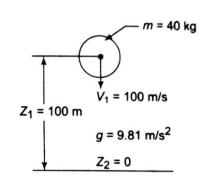
Solution Since the only force is that due to gravity,

$$\frac{1}{2}mV_2^2 + mgz_2 = \frac{1}{2}mV_1^2 + mgZ_1$$

$$V_2 = \sqrt{2gz_1 + V_1^2}$$

$$= \sqrt{2 \times 9.81 \times 100 + 100^2}$$

$$= 104.4 \text{ m/s} \qquad \text{Ans.}$$



The velocity increases, as expected, and the magnitude is independent of the mass of the object.

Example 3.2 Gas from a bottle of compressed helium is used to inflate an inelastic flexible balloon, originally folded completely flat to a volume of 0.5 m³. 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.

[LO 3.3]

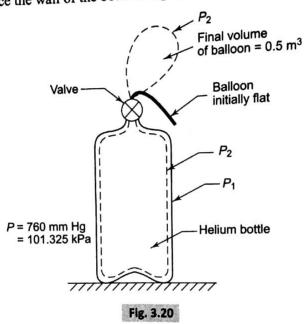
Levels of Difficulty

- Low complexity: Level 1 and Level 2 Category
- Medium complexity: Level 3 and Level 4 Category
- High complexity: Level 5 and Level 6 Category

Solution The firm line P_1 (Fig. 3.20) shows the boundary of the system before the process, and the dotted line P_2 shows the boundary after the process. The displacement work

$$W_d = \int_{\text{Balloon}} pdV + \int_{\text{Bottle}} pdV = p \Delta V + 0$$
$$= 101.325 \frac{\text{kN}}{\text{m}^2} \times 0.5 \text{ m}^3 = 50.66 \text{ kJ}$$

This is positive, because work is done by the system. Work done by the atmosphere is -50.66 kJ. Since the wall of the bottle 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 50.66 kJ by an amount equal to the work done in stretching the balloon, although

the displacement work done by the atmosphere is still -50.66 kJ. However, if the system includes both the gas and the balloon, the displacement work would be 50.66 kJ, as estimated above.

E) Example 3.3 When the valve of the evacuated bottle (Fig. 3.21) is opened, atmospheric air rushes into it. If the atmospheric pressure is 101.325 kPa, and 0.6 m3 of air (measured at atmospheric conditions) enters into the bottle, calculate the work done by air. [LO 3.2]

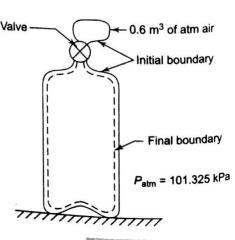


Fig. 3.21

[LO 3.5]

The displacement work done by air Solution

$$W_d = \int_{\text{Bottle}} p dV + \int_{\text{Free-air boundary}} p dV$$
$$= 0 + p \Delta V$$
$$= 101.325 \text{ kN/m}^2 \times 0.6 \text{ m}^3 = 60.8 \text{ kJ}$$

Since the free-air boundary is contracting, the work done by the system is negative (ΔV) being negative), and the surroundings do positive work upon the system.

(M) Example 3.4 A 2 kW, 25 litre storage water heater is used to raise the temperature of incoming cold water to a desired pre-set end use temperature ranging from 25°C to 75°C. Assume that all the electrical energy has gone into heating the water. If the cold water temperature is 15°C and the end use temperature is 50°C, determine the time required to reach the end use temperature after the heater is switched on. The heat capacity c, for water is 4.2 kJ/kgK and density of water is [LO 3.9] 1000 kg/m³.

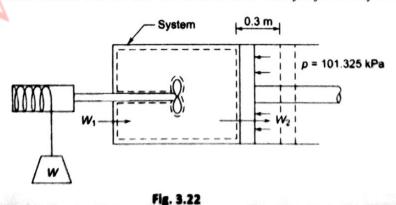
Solution Mass of water in the heater is $25 \times 10^{-3} \times 1000 = 25$ kg Heat required to raise the temperature of water from 15°C to 50°C is

$$Q = 25 \times 4.2(50 - 15) = 3675 \text{ kJ}$$

Energy input to the water per minute is $= 2 \text{ kJ/s} \times 60 \text{ s} = 120 \text{ kJ}$ Time required to raise the temperature is

$$=\frac{3675}{120}$$
 minutes = 30.625 minutes

(M) Example 3.5 A piston and cylinder machine containing a fluid system has a stirring device in the cylinder (Fig. 3.22). The piston is frictionless. and it is held down against the fluid due to the atmospheric pressure of 101.325 kPa. The stirring device is turned 10,000 revolutions with an average torque against the fluid of 1.275 mN. Meanwhile the piston of 0.6 m diameter moves out 0.8 m. Find the net work transfer for the system.



Solution Work done by the stirring device upon the system (Fig. 3.22)

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$$W_1 = 2\pi TN$$

= $2\pi \times 1.275 \times 10.000 \text{ Nm} = 80 \text{ k J}$

Work done by the system upon the surroundings

$$W_3 = (pA) \cdot L$$

= 101.325 $\frac{\text{kN}}{\text{m}^2} \times \frac{\pi}{4}$ (0.6)² m² × 0.80 m = 22.9 kJ

This is positive work for the system. Hence, the net work transfer for the $W = W_1 + W_2 = -80 + 22.9 = -57.1 \text{ kJ}$ system

The following data refer to a 12-cylinder, single-acting, (M) Example 3.6 two-stroke marine diesel engine:

Speed-150 rpm

Cylinder diameter -0.8 m

Stroke of piston-1.2 m

Area of indicator diagram—5.5 \times 10⁻⁴ m²

Length of diagram-0.06 m

Spring value—147 MPa per m

Find the net rate of work transfer from the gas to the pistons in kW.

[LO 3.4]

Mean effective pressure, p_m , is given by

$$p_{m} = \frac{a_{d}}{l_{d}} \times \text{spring constant}$$

$$= \frac{5.5 \times 10^{-4} \text{ m}^{2}}{0.06 \text{ m}} \times 147 \frac{\text{MPa}}{\text{m}} = 1.35 \text{ MPa}$$

One engine cycle is completed in two strokes of the piston or one revolution of the crank-shaft.

.. work done in one minute

$$= p_m LAN$$

= 1.35 × $\frac{\pi}{4}$ (0.8)² × 1.2 × 150 = 122 MJ

Since the engine is single acting, and it has 12 cylinders, each contributing an equal power, the rate of work transfer from the gas to the piston is given by

(H) Example 3.7 It is required to melt 5 tonnes/h of iron from a charge at 15°C to molten metal at 1650°C. The melting point is 1535°C and the latent heat is 270 kJ/kg. The specific heat in solid state is 0.502 and in liquid state (29.93/atomic weight) kJ/kg K. If an electric furnace has 70 percent efficiency, find the kW rating needed. If the density in molten state is 6900 kg/m³ and the bath volume is three times the hourly melting rate, find the dimensions of the cylindrical furnace if the length to diameter ratio is 2. The atomic weight of iron

[LO 3.8]

Heat required to melt 1 kg of iron at 15°C to molten metal at 1650°C = Heat required to raise the temperature from 15°C to 1535°C + Latent heat + Heat required to raise the temperature from 1535°C to 1650°C

Melting rate = 5×10^3 kg/h

So, the rate of heat supply required

$$= (5 \times 10^3 \times 1094.5) \text{ kJ/h}$$

Since the furnace has 70 percent efficiency, the rating of the furnace would be

$$= \frac{\text{Rate of heat supply per second}}{\text{Furnace efficiency}}$$

$$= \frac{5 \times 10^3 \times 1094.5}{0.7 \times 3600} = 217 \times 10^3 \text{ kW}$$
Volume needed = $\frac{3 \times 5 \times 10^3}{6900} \text{ m}^3 = 2.18 \text{ m}^3$

If d is the diameter and l the length of the furnace

or
$$\frac{\pi}{4} d^2 l = 2.18 \text{ m}^3$$

$$\frac{\pi}{4} d^2 \times 2d = 2.18 \text{ m}^3$$

$$d = 1.15 \text{ m}$$

$$l = 2.30 \text{ m}$$

M Example 3.8 If it is desired to melt aluminium with solid state specific heat 0.9 kJ/kg K latent heat 390 kJ/kg, atomic weight 27, density in molten state 2400 kg/m³ and final temperature 700°C, find out how much metal can be melted per hour with the above kW rating. Other data are as in the above example. Also, find the mass of aluminium that the above furnace will hold. The melting point of aluminium is 660°C. [LO 3.8]

Solution Heat required per kg of aluminium

=
$$0.9 (660 - 15) + 390 + \frac{29.93}{27} (700 - 660)$$

= $580.5 + 390 + 44.3 = 1014.8 \text{ kJ}$
= $\frac{1014.8}{0.7} = 1449.7 \text{ kJ/kg}$

Heat to be supplied

With the given power, the rate at which aluminium can be melted

$$= \frac{217 \times 10^3 \times 3600}{1449.7} \text{ kg/h} = 5.39 \text{ tonnes/h}$$

Mass of the aluminium that can be held in the above furnace $= 2.18 \times 2400 \text{ kg} = 5.23 \text{ tonnes}$

HExample 3.9 A cooling tower nozzle disperses water into a stream of droplets. If the average diameter of the droplets is 60 microns, estimate the work required for atomizing 1 kg of water isothermally at the ambient conditions. Given: surface tension of water in contact with air = 0.07 N/m, density of water = 1000 kg/m³. Water is assumed to enter the nozzle through a pipe of 15 mm diameter. [LO 3.6]

E Example 3.14 A piston-cylinder device operates 1 kg of fluid at 20 atm. pressure. The initial volume is 0.04 m3. The fluid is allowed to expand reversibly following a process $pV^{1.45}$ = constant so that the volume becomes double. The fluid is then cooled at constant pressure until the piston comes back to the original position. Keeping the piston unaltered, heat is added reversibly to restore it to the initial pressure. Calculate the work done in the cycle. [LO 3.3]

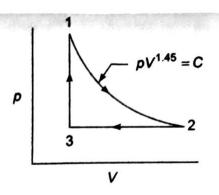


Fig. 3.23

Solution

$$\begin{aligned} p_1 &= 20 \text{ atm} = 20 \times 1.01325 = 20.265 \text{ bar} \\ V_1 &= 0.04 \text{ m}^3, \ V_2 = 2V_1 = 0.08 \text{ m}^3 \\ p_2 &= (V_1/V_2)^n \cdot p_1 = (1/2)^{1.45} \times 20.265 \\ &= 7.417 \text{ bar} \\ W_{1-2} &= \frac{p_1 V_1 - p_2 V_2}{n-1} = \frac{100 \left[20.265 \times 0.04 - 7.417 \times 0.08 \right]}{0.45} \\ &= 47.82 \text{ kJ} \\ W_{2-3} &= p_2 \left(V_2 - V_1 \right) = -100 \times 0.04 \times 7.417 = -29.65 \text{ kJ} \\ \text{Work in the cycle} &= 47.82 - 29.65 = 18.17 \text{ kJ} \end{aligned}$$