

INTRODUCTION TO THERMODYNAMICS

"Software is like entropy. It is difficult to grasp, weighs nothing and obeys the second law of thermodynamics ; it always increases."

— Norman Ralph Augustine

The term thermodynamics is derived from the Greek word therme (heat) and dynamics (power or motion), thus thermodynamics means that heat power or heat in motion.

Thermodynamics is defined as the science of engineering that deals with the storage of energy, entropy, heat and work, mutual conservation of heat and work, exchange of energy and those properties of substances that govern the relation between heat and work.

From the time, man created fire by striking flint stones, it was known that

- (a) fire is hot
- (b) its hotness can change

These observations have given rise to the terms heat (hotness), temperature (the degree of hotness) and creation of heat by friction.

Thermodynamics explains these observations on scientific basis by :

- ❖ Logically developing a quantitative relation between (frictional) workdone by dissipation and energy stored (First law of Thermodynamics)
- ❖ Defining and showing how to measure heat (First law of thermodynamics)
- ❖ Defining the concept of temperature (Zeroth law of thermodynamics)
- ❖ Showing how to measure temperature (Second law of thermodynamics)
- ❖ Logically developing criteria for inter-conversion of work and heat (Second law of thermodynamics)

1.1 THE CONTINUUM MODEL

Matter may be described at a molecular (or microscopic) level using the techniques of statistical mechanics and kinetic theory. For engineering purposes, however, we want "averaged" information i.e., a macroscopic, not a microscopic description. There are two reasons for this. First a microscopic description of an engineering device may produce too much information to manage. For example, 1 mm^3 of air at standard temperature and pressure (S.T.P.) contains 10^{16} molecules, each of which has a position and a velocity. Typical engineering applications involve more than 10^{20} molecules. Second, and more importantly, microscopic positions and velocities are generally not useful for determining how macroscopic systems will act or react unless, for instance, their total effect is integrated. We therefore neglect the fact that real substances are composed of discrete molecules and model matter from the start as a smoothed-cut continuum. The information we have about a continuum represents the microscopic information averaged over a volume. Classical thermodynamics is concerned only with continua.

1.2 PRINCIPAL CONCEPTS OF THERMODYNAMICS

Followings principal concept of thermodynamics are discussed below :

1.2.1 System

A thermodynamic system is a quantity of matter of fixed identity, around which we can draw a boundary as shown in Figs. 1.1 and 1.2.

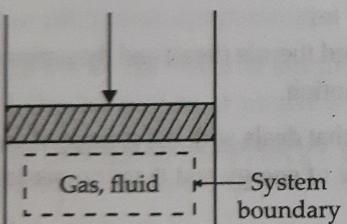


Fig. 1.1 Piston (boundary) and gas (system).

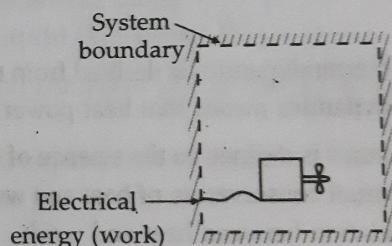


Fig. 1.2 Boundary around electric motor (system).

The boundaries may be fixed or movable. Work or heat can be transferred across the system boundary. Everything outside the boundary is the surroundings. When working with devices such as engines it is often useful to define the system to be identifiable volume with flow in and out. This is termed a control volume. An example is shown in Fig. 1.3.

A closed system is a special class of system with boundaries that matter cannot cross. Hence the principle of the conservation of mass is automatically satisfied whenever we employ a closed system analysis. This type of system is sometimes termed as a control mass.

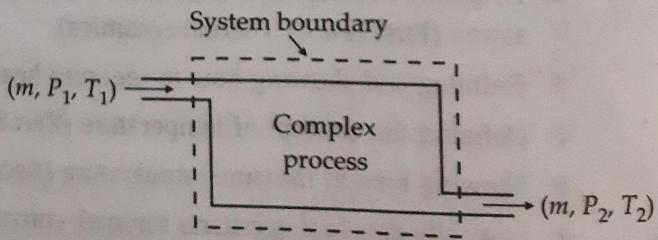


Fig. 1.3 Sample control volume.

1.2.2 State

The thermodynamic state of a system is defined by specifying values of a set of measurable properties sufficient to determine all other properties. For fluid systems, typical properties are pressure, volume and temperature. More complex system may require the specifications of more usual properties. As an example, the state of an electric battery requires the specification of the amount of electric charge it contains.

Properties may be **extensive** or **intensive**. Extensive properties are additive. Thus, if the system is divided into a number of sub-systems, the value of property for the whole system is equal to the sum of the values for the parts. *Volume* is an extensive properties. Intensive properties do not depend on the quantity of matter present. Temperature and pressure are intensive properties.

Specific properties are extensive properties per unit mass and are denoted by lower case (small) letters. *For example,*

$$\text{Specific volume} = V/m = v \quad \dots(1.1)$$

Specific properties are intensive because they do not depend on the mass of the system.

The properties of a simple system are uniform throughout. In general, however, the properties of a system can vary from point to point. We can analyse a general system by sub-dividing it (either conceptually or in practice) into number of simple systems in each of which the properties are assumed to be uniform.

It is important to note that the properties describe states only when the system is in equilibrium.

1.2.3 Equilibrium

The state of a system in which properties have definite, unchanged values as long as external conditions are unchanged is called an equilibrium state. The mechanical and thermal equilibrium are shown in Fig. 1.4.

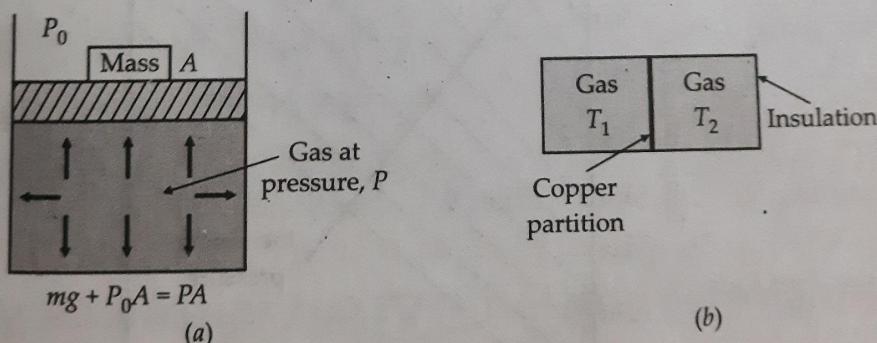


Fig. 1.4 (a) Mechanical equilibrium, (b) Thermal equilibrium.

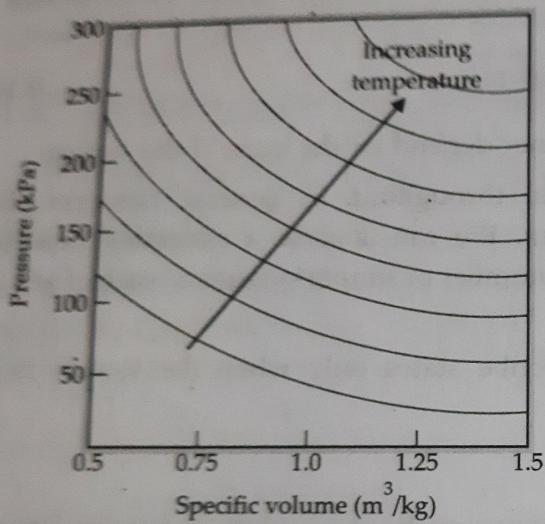
If a system is simultaneously in a state of mechanical equilibrium (no unbalance forces), thermal equilibrium (no temperature differences) and chemical equilibrium, then system is said to be in thermodynamics equilibrium.

1.2.4 Process

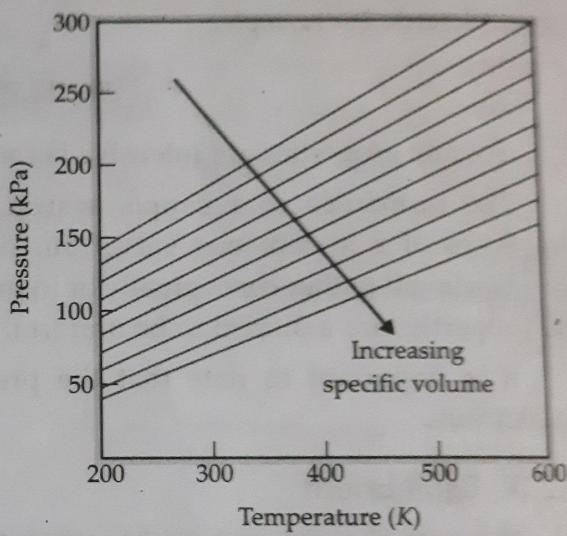
If the state of a system changes, than it is undergoing a **process**. The succession of states through which the system passes defines the **path** of the process. If, at the end of the process, the properties have returned to their original values, the system has undergone a **cyclic process** or a **cycle**. Note that even if a system has returned to its original state and completed a cycle, the state of the surroundings may have changed.

Quasi-Equilibrium Processes

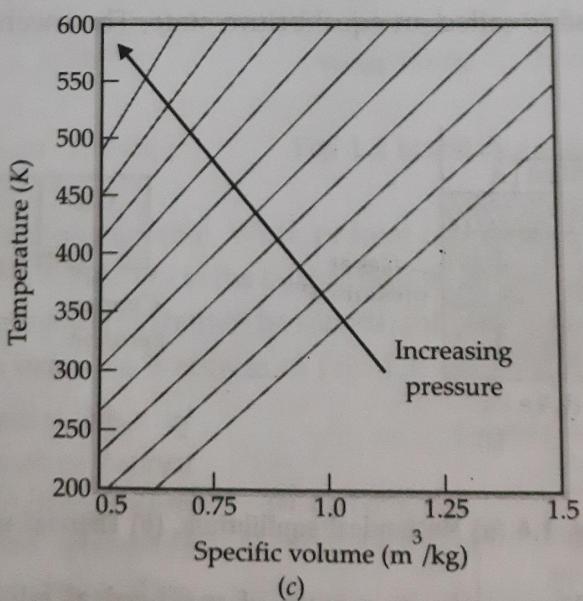
Generally, we are often interested in charting thermodynamic processes between states on thermodynamic coordinates. As we have already discussed under section 1.2.2 i.e., about 'state', however, that properties define a state only when a system is in equilibrium. If a process involves finite, unbalanced forces, the system can pass through non-equilibrium state, which we cannot treat.



(a)



(b)



(c)

Fig. 1.5 Thermodynamic coordinates and isolines for an ideal gas
(a) $P - v$ diagram, (b) $P - T$ diagram, (c) $T - v$ diagram.

An extremely useful idealization, however, is that only "infinitesimal" unbalanced forces exist, so that the process can be viewed as taking place in a series of "Quasi-equilibrium" states. (The term 'quasi' can be taken to mean as if, one will see it used in a number of contexts such as quasi-one-dimensional, quasi-steady etc.). For this to be true the process must be slow in relation to the time needed for the system to come to equilibrium internally. For a gas at conditions of interest to us, a given molecule can undergo roughly 10^{10} molecular collisions per second, so that, if ten collisions are needed to come to equilibrium, the equilibration time is on the order of 10^{-9} s (ns). This is generally much shorter than the time scales associated with the bulk properties of the flow (say to time needed for a fluid particle to move some significant fraction of the length of the device of interest). Over a large range of parameters, therefore, it is a very good approximation to view the thermodynamic processes as consisting of such a succession of equilibrium, which we can plot as in Fig. 1.5.

Figure 1.5 demonstrates the use of thermodynamic coordinates to plot isolines, lines along which a property is constant. They include **constant temperature lines, or isotherms** on a ***P-v* diagram**, **constant volume lines, or isochors** on a ***T-P* diagram** and **constant pressure lines or isobars** on a ***T-v* diagram** for an ideal gas.

1.2.5 Equation of State

It is an experimental fact that two properties are needed to define the state of any pure substance in equilibrium or undergoing a steady or quasi-steady process. Thus for a simple compressible gas like air

$$P = P(v, T), \quad \text{or} \quad v = v(P, T) \quad \text{or} \quad T = T(P, v) \quad \dots(1.2)$$

where v is volume per unit mass.

In words if we know v and T , we know P etc.

Any of these is equivalent to an equation $f(P, v, T) = 0$, which is known as an **equation of state**.

The equation of state for an ideal gas, which is a very good approximation to real gases at conditions that are typically of interest for aerospace applications, is

$$P\bar{v} = RT \quad \dots(1.3)$$

where \bar{v} is the volume per mole of gas and R is 'Universal Gas Constant' i.e., 8.31 kJ/k mol-K.

A form of this equation, which is more useful in fluid flow problems is obtained if one divides by molecular weight M .

$$Pv = RT \quad \text{or} \quad P = \rho RT \quad \dots(1.4)$$

1.3 THERMAL EQUILIBRIUM AND ZERO TH LAW OF THERMODYNAMICS

The concept of temperature originated in man's primitive perceptions of hot and cold. These perceptions are subjective and limited in range. The precise definition of *temperature* is a consequence of the zeroth law of thermodynamics.

Let us consider a simple homogeneous system of constant mass, as for example, a fluid. Experiment shows that for a given composition of a fluid the values of its pressure P , and its

volume V are sufficient to specify completely its state of equilibrium. The P and V are independent variables, i.e., if the volume is kept constant, the pressure may vary widely over a range of values or vice versa. Let us consider two systems A and B , each being enclosed by isolating walls as shown in Fig. 1.6(a). A state of equilibrium of a system is defined as one in which the thermodynamic coordinates are constant with time, so long as the surrounding do not change. A and B being isolated systems do not interact with the surroundings; each is in a state of thermodynamic equilibrium.

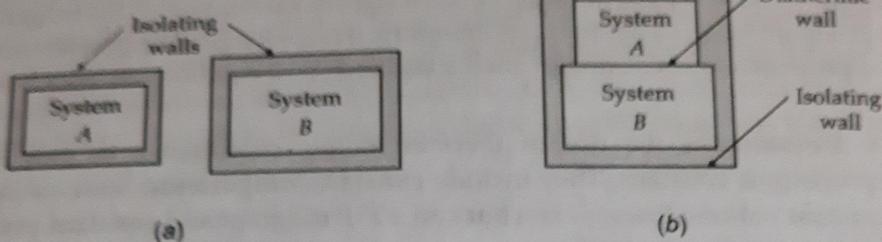


Fig. 1.6 (a) Systems A and B isolated from each other. (b) Systems A and B in thermal contact.

Now A and B are brought into thermal contact by means of a diathermal wall as shown in Fig. 1.6(b). When both systems will, in general, undergo spontaneous changes in their physical properties until the combined system of A and B attains a new state of equilibrium when no further changes occur. The two systems A and B are then said to be in *thermal equilibrium* with each other. Before they were brought into contact with each other A and B were isolated as shown in Fig. 1.6(b) and the pairs of variables P_A, V_A for A and P_B, V_B for B can take any arbitrary attainable values quite independently each other. When they are in thermal equilibrium with each other the situation is altered so that only three of the variables are independent, the fourth being determined by the other three. As discussed above that A and B are under the constraint of being in thermal equilibrium with each other, there is one relation between the four variables which may be written as :

$$\phi(P_A, V_A, P_B, V_B) = 0 \quad \dots(1.5)$$

where ϕ is some function whose form depends on the fluids A and B .

Thermal equilibrium is the state attained by two or more systems after they have been in thermal contact with each other by means of diathermal walls and characterized by restricted values of the thermodynamic coordinates.

The Zeroth Law of Thermodynamics :
Empirical Temperature Statement. If two systems A and B are in thermal equilibrium with a third system C , then they (all three A , B and C) are in equilibrium with each other. (see Fig. 1.7)

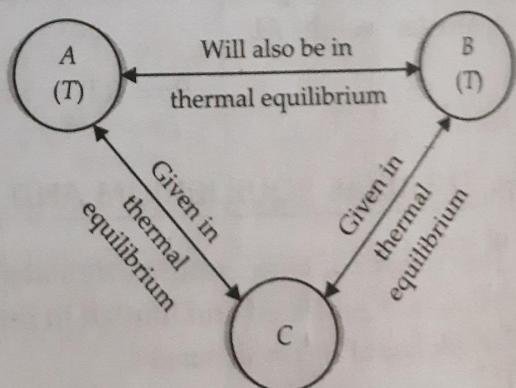


Fig. 1.7 Zeroth law of thermodynamics

The zeroth law allows one to other systems according to direction heat flows when two systems are put into thermal contact. One system is said to be hotter than another if heat flows from the former to the later when they are put into thermal contact. This allows us to introduce a new parameter called an *empirical temperature*, which is the same for all bodies that are in thermal equilibrium with each other. This is done by constructing one system, called a *thermometer*, that allows one to ascribe a number to the temperature, e.g., the height of a coloured liquid in a glass tube.

This law simply states a fact of experience. From the statement it is clear that three systems must have same property in common ; the common property is identified as *temperature*. The condition under which system *A* and system *C* are in thermal equilibrium is expressed by the equation

$$\phi_1(P_A, V_A, P_C, V_C) = 0 \quad \dots(1.6)$$

or

$$P_C = F_1(P_A, V_A, V_C)$$

where F_1 is another function.

Similarly, system *B* is in thermal equilibrium with system *C*, then

$$\phi_2(P_B, V_B, P_C, V_C) = 0 \quad \dots(1.7)$$

or

$$P_C = F_2(P_B, V_B, V_C)$$

$$\text{Hence } F_1(P_A, V_A, V_C) = F_2(P_B, V_B, V_C) \quad \dots(1.8)$$

The zeroth law may then be expressed as

$$\phi_3(P_A, V_A, P_B, V_B) = 0 \quad \dots(1.9)$$

In terms of the law, Eqs. (1.8) and (1.9) are equivalent, but while Eq. (1.8) contains V_C while Eq. (1.9) does not. It follows that F_1 and F_2 must contain V_C in such a form that it cancels out in Eq. (1.8). When this cancellation is carried out, Eq. (1.8) reduces to

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B) \quad \dots(1.10)$$

Applying the same argument, since system *A* and system *C* are separately in equilibrium with system *B*, it follows that

$$\phi_1(P_A, V_A) = \phi_3(P_C, V_C) \quad \dots(1.11)$$

$$\text{Therefore, } \phi_1(P_A, V_A) = \phi_2(P_B, V_B) = \phi_3(P_C, V_C) = T \quad \dots(1.12)$$

Thus for every system there exists a function of its state variables such that the numerical value of the function is same for all systems in thermal equilibrium with each other. The common value T of these functions is called *empirical temperature*. Temperature may be defined as a function of state of a system such that it takes the same value for all systems in thermal equilibrium with one other.

For a sample system $\phi(P, V)$, T is called the *equation of state*.

1.4 EQUIVALENCE OF HEAT AND WORK

According to thermodynamics, heat is a form of energy. Heat can, therefore be converted into mechanical work and vice versa. For example, liquids get heated by compression of a gas ; make it hot, heat is produced by rubbing of hands and sparks are produced when a stone is hammered. In brief, we may say that, work is the energy exchanged between a system and surroundings due to change in volume of the system. On the other hand, any device which converts heat energy into mechanical work is known as a *heat engine*. Steam engine, diesel engine and petrol engine are the examples of heat engines.

Joule established a relation between workdone W and heat produced Q . According to him ; whenever work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.

$$W \propto Q$$

$$W = JQ$$

...(1.13)

or

where J is a constant known as *Joule's mechanical equivalent of heat*.

$$\text{If } Q = 1, W = J$$

The mechanical equivalent of heat is, therefore, defined as the amount of work done in producing a unit quantity of heat.

If Q is measured in calories and W in Joule, then $J = 4.18 \text{ J/cal}$.

In SI unit both W and Q are measured in Joules, then

$$W = Q$$

...(1.14)

Example 1.1 The height of Niagara falls is 50 m. Calculate the difference between the temperature of water at the top and at the bottom of the fall, if $J = 4.2 \text{ J/cal}$.

Solution. Given

$$h = 50 \text{ m}, g = 9.8 \text{ m/s}^2, s = 1 \text{ kcal/kg}^\circ\text{C}, J = 4.2 \text{ J/cal.}$$

Suppose m kg of water falls in one second. The potential energy lost in one second is

$$W = mgh = m \times 9.8 \times 50 \text{ J}$$

This lost energy is converted into heat. If Q be the heat produced, then

$$Q = \frac{W}{J} = \frac{m \times 9.8 \times 50}{4.2} = 117 \text{ m cal} = 0.117 \text{ m kcal}$$

If this heat causes a temperature rise ΔT in water, then

$$Q = \text{mass} \times \text{specific heat of water} \times \text{temperature rise}$$

$$0.117 \text{ m} = m \times 1 \times \Delta T$$

$$\Delta T = 0.117^\circ\text{C.}$$

1.5 WORK DONE BY A THERMODYNAMIC SYSTEM

The term work refer to an interchange of energy between system and its surroundings. If a force \mathbf{F} produces an infinitesimal displacement dx , then the workdone by the force is

$$dW = \mathbf{F} \cdot dx \quad \dots(1.15)$$

If a force is exerted by the system as a whole on its surrounding and a displacement takes place, the workdone either by the system or on the system is called *external work*.

For example, a gas contained in cylinder at a uniform pressure while expanding pushes the piston out and does external work on its surroundings. On the other hand, the work done by one part of the system on the another part of the same system is called the *internal work*. For example, in an actual gas there exist intermolecular attractions and when such a gas expands, the work is done against these mutual attractions between the molecules, which is the *internal work*. Thus interactions of the molecules of a system constitute internal work.

Suppose, we now try to compute the workdone W for a specific thermodynamic process. Consider a constant mass of a gas in a cylindrical container with movable piston and cylinder as the surroundings. Let initially the system be in equilibrium with its surroundings and has a pressure P_i and volume V_i . Heat can flow into the system or out of it through the walls and work can be done by having the piston compressed or work can be done on the system by expanding against the piston. Consider some process where the system interacts with its surroundings and reaches a final equilibrium state characterized by a pressure P_f and volume V_f .

Suppose the gas is expanding against the piston (see Fig. 1.8). The workdone by the gas is displacing the piston through an infinitesimal displacement dx is given by

$$dW = Fdx \quad \dots(1.16)$$

where F is the force exerted by the gas on the piston.

If A is the area of the piston and P the pressure at the instant when displacement dx is taking place.

$$dW = PAdx = PdV \quad \dots(1.17)$$

where $dV (= Adx)$ is the differential increase in the volume of the gas.

In general the pressure varies during a displacement and we must know how P varies with displacement.

The total workdone W by the gas on the piston is found by the integration

$$W = \int dW = \int_{V_i}^{V_f} PdV \quad \dots(1.18)$$

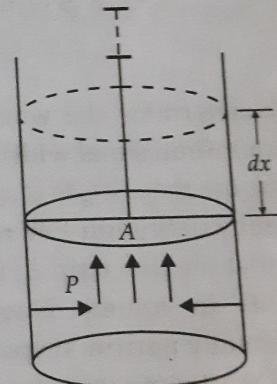


Fig. 1.8 Expansion of gas.

1.6 INDICATOR DIAGRAM

The thermodynamic state of a system can be represented by its pressure P and volume V . If the gaseous system undergoes a change, it passes through various values of P and V . These changes can be depicted on a P - V graph (Fig. 1.9) in which volume V is taken along abscissa (X-axis) and the pressure P is taken along the ordinate (Y-axis). Various states of the gas can be represented by point in Fig. 1.9. A curve joining these points will represent the entire change or process. A curve representing the changes in the thermodynamic state of a system on P - V graph is called the *indicator diagram* for the system. These indicator diagrams help in calculating the workdone in the processes in which a direct mathematical relation does not exist between P and V . In such cases the *workdone is equal to the area enclosed by the P - V diagram and the volume axis*.

Suppose a cylinder fitted with a movable piston is filled with an ideal gas. Let the initial pressure and volume of the gas be P_i and V_i respectively. When heated, the gas expands and pushes the piston and finally its volume becomes V_f and pressure becomes P_f . The change in the state of the gas is shown in indicator diagram in (Fig. 1.9). The initial state of the gas is represented by point $A(P_i, V_i)$ and final state by $B(P_f, V_f)$.

Then work done in this process is

$$W = \int_{V_i}^{V_f} P dV \quad \dots(1.19)$$

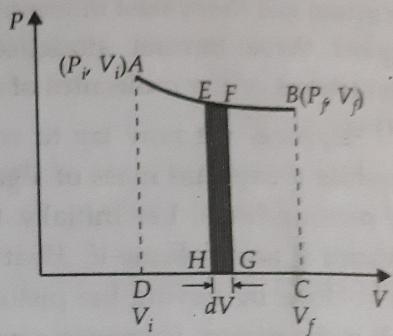


Fig. 1.9 Indicator diagram.

To determine the work done in the process using the indicator diagram, consider a strip $EFGH$ of infinitesimal width dV at point E of P - V graph. Since E and F are infinitesimally close, we may assume that $EFGH$ is a rectangle i.e., pressure P at E and F are equal. The area of this strip is PdV . But by definition PdV represents the amount of workdone in small change in volume dV . This means that the fine strip $EFGH$ on P - V graph represents the amount of workdone in infinitesimal change dV in volume. Now, we can divide the entire P - V graph in a very large number of infinitesimally narrow strips and find area of each strip. The sum of all these areas will be equal to the total workdone in change of state of the gas from point A to point B .

$$\begin{aligned} W &= \text{Sum of areas of infinitesimal narrow strips} \\ &= \sum P dV = \text{Area } ABCD \end{aligned}$$

which in turn can be written as

$$W = \int_{V_i}^{V_f} P dV = \text{Area of } PV\text{-graph} \quad \dots(1.20)$$

Thus the area of P - V graph gives the amount of workdone in the process. It may be noted that if the volume of the gas increases in the process, the workdone is positive and if the volume decreases then the workdone is negative.

1.7 HEAT AND WORK-PATH FUNCTIONS

Thermodynamic properties like pressure, volume, temperature and entropy are point functions i.e., for a given point on a diagram there is a definite value of each property corresponding to the point. The differentials of point functions are exact differentials.

Let P_1 and V_1 be the pressure and volume of a gas in the initial state 1 and P_2 and V_2 the corresponding values in the final state 2 as shown in the P - V diagram (see Fig. 1.10). The change in volume is given by

$$\int_1^2 dV = V_2 - V_1 \quad \dots(1.21)$$

In other words, the change in volume depends only on the value of V in the initial and final states and is independent of the paths.

On the other hand work is a path function. The workdone in a quasistatic process between two given states depends upon the path followed and is an inexact differential.

It has been proved that the workdone when the changes take place along the path A is given by area $1A2V_2V_1$. When the change takes place along the path B the work done is given by the area $1B2V_2V_1$. This shows that the workdone depends upon the path taken by the process.

\therefore For the path A

$$W_A = \int_{1A}^{2A} \delta W = \int_{1A}^{2A} PdV \quad \dots(1.22)$$

and for the path B

$$W_B = \int_{1B}^{2B} \delta W = \int_{1B}^{2B} PdV \quad \dots(1.23)$$

The values of W_A and W_B are not equal, hence work cannot be expressed as the difference between the values of some property of the system in the initial and final states.

Heat is also a path function. The amount of heat transferred when a system changes from state 1 to state 2 depends on the intermediate state i.e.,

$$W_A = \int_1^2 \delta W = _1Q_2 \quad \dots(1.24)$$

where $_1Q_2$ represents the heat transferred during the given process between the states 1 and 2.

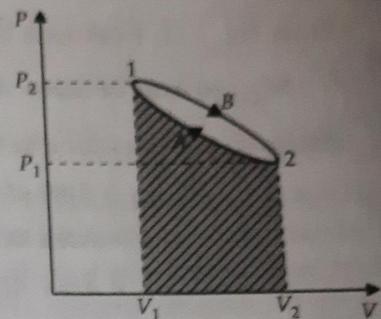


Fig. 1.10 P - V diagram for work-path function.

1.8 WORK DONE IN CYCLIC PROCESS

When a system after passing through a series of changes return to its initial state, the process is known as *cyclic process*. In Fig. 1.11, ABCDA is a cyclic process in which the system starting from its initial state A reaches a state C via the path ABC and then returns to initial state A via the path CDA.

From Fig. 1.11, workdone in the change ABC,

$$W_{ABC} = \text{Area of curve } ABC = \text{Area } ABCC'A'A$$

Similarly, the workdone in the change CDA

$$\begin{aligned} W_{CDA} &= \text{Area of curve } CDA \\ &= \text{Area } CC'A'ADC \\ &= \text{Area } ADCC'A'A \end{aligned}$$

Therefore, the net workdone in the complete cycle is

$$\begin{aligned} W &= W_{ABC} - W_{CDA} \\ &= \text{Area } ABC'A'A - \text{Area } ADCC'A'ADC \\ &= \text{Area } ABCDA \end{aligned} \quad \dots(1.25)$$

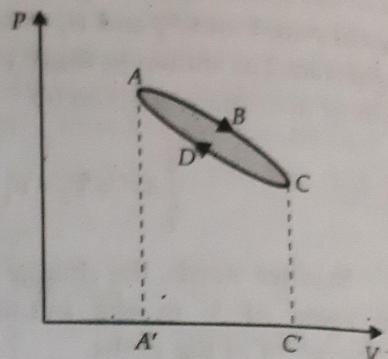


Fig. 1.11 Cyclic process.

This is shown by shaded region in Fig. 1.11.

Obviously, the P-V curve for a cyclic process is a closed curve and the workdone in such a process is equal to the area enclosed by the PV-graph. As per convention the work done by the system is treated as positive and the workdone on the system is negative. In case of cyclic process the convention is modified as follows :

If in a cyclic change, the P-V graph is traced in the clockwise direction, the net amount of workdone is positive and if the curve is traced in the anticlockwise direction, the workdone is negative ; and is done on the system.

1.9 WORK DONE IN CERTAIN PROCESS

1.9.1 Isothermal Process

In a *isothermal process* the temperature of the system remains constant throughout the change.

Work is done by a gas when it is allowed to expand isothermally.

Let the initial and final volumes be V_1 and V_2 respectively. As before, the workdone for a very small change in volume dV

$$dW = PdV$$

when gas expands from volume V_1 to V_2

Workdone

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

Since expansion is isothermal

$$PV = RT \quad \text{or} \quad P = \frac{RT}{V}$$

$$W = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \log_e \frac{V_2}{V_1}$$

or

$$W = 2.3026 RT \log_{10} \frac{V_2}{V_1} \quad \dots(1.26)$$

1.9.2 Adiabatic Process

In adiabatic process, during the change of state the system is not allowed to exchange heat with surroundings. This is done either by thermally insulating the system from the surroundings by the use of insulating materials or by performing the process so rapidly that gas does not find time to exchange heat. In the adiabatic process, the internal energy of gas remains constant.

Suppose 1 g mole of a perfect gas is enclosed in a cylinder having perfectly insulating walls. Let the gas expands adiabatically from initial pressure P_1 and volume V_1 at point A to final pressure P_2 and volume V_2 at point B as shown in Fig. 1.12.

Then the workdone by the gas during this expansion is given by

$$W = \int_{V_1}^{V_2} P dV = \text{Area } ABCD$$

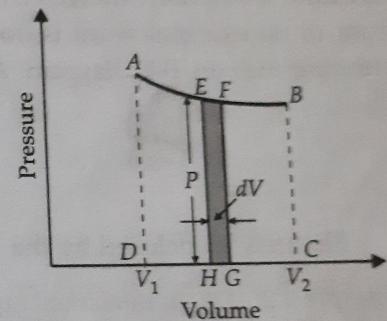


Fig. 1.12 Indicator diagram.

During an adiabatic process

$$PV^\gamma = K (\text{constant})$$

$$P = \frac{K}{V^\gamma}$$

Therefore,

$$W = \int_{V_1}^{V_2} K \frac{dV}{V^\gamma} = K \int_{V_1}^{V_2} V^{-\gamma} dV = K \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2} = \frac{K}{1-\gamma} \left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right]$$

But A and B lie on the same adiabatic curve,

Hence

$$P_1 V_1^\gamma = P_2 V_2^\gamma = K$$

$$W = \frac{1}{1-\gamma} \left[\frac{P_2 V_2}{V_2^{\gamma-1}} - \frac{P_1 V_1}{V_1^{\gamma-1}} \right]$$

$$= \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1]$$

..(1.27)

1.9.3 Isobaric Process

If the gas enclosed in a container expands in such a manner that its pressure remains constant, the process is called an *isobaric process*.

Let the initial and final volumes of one gm mole of a perfect gas enclosed in an expanding chamber in which the pressure is kept constant. The workdone for a very small change in volume dV

$$dW = PdV$$

When the gas expands from V_1 to V_2

$$\text{Work done } W = \int_{V_1}^{V_2} PdV = P(V_2 - V_1) \quad \dots(1.28)$$

Because the pressure is kept constant in an isobaric process.

1.9.4 Isochoric Process

In an *isochoric process*, the state of gas changes in such a manner that its volume remains constant. Obviously, there is a change in the pressure of the gas when heat is given to it or taken from it, no external work is done. The isochoric process is represented by a line parallel to the pressure axis on *P-V* diagram. As $dV = 0$,

$$W = \int_{V_1}^{V_2} PdV = 0 \quad \dots(1.29)$$

No area is enclosed by the *P-V* diagram.

Example 1.2 If in an isothermal expansion the volume of 1 g mole of a gas at $27^\circ C$ is doubled, calculate the workdone in the process. ($R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$).

Solution. Given $T = 27^\circ C = 300 \text{ K}$, $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$, $V_2 = 2V_1$

The workdone in isothermal process is

$$\begin{aligned} W &= 2.3026 RT \log_{10} \frac{V_2}{V_1} \\ &= 2.3026 \times 8.3 \times 300 \log_{10} \frac{2V}{V} \\ &= 2.3026 \times 8.3 \times 300 \times 0.3010 = 1725.8 \text{ J.} \end{aligned}$$

Example 1.3 A definite mass of a perfect gas is compressed adiabatically to half of its original volume. Determine the resultant pressure if the initial pressure was 1 atmosphere. [$\gamma = 1.4$ and $2^{1.4} = 2.64$]

Solution. Given $P_1 = 1 \text{ atmosphere}$, $V_2 = \frac{V_1}{2}$, $\gamma = 1.4$ and $2^{1.4} = 2.64$

For an adiabatic change

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$\therefore P_2 = P_1 \left[\frac{V_1}{V_2} \right]^\gamma = 1 \times \left[\frac{V_1}{V_1/2} \right]^{1.4} = 1 \times (2)^{1.4} = 2.64 \text{ atmosphere.}$$

1.10 INTERNAL ENERGY

The energy possessed by a body or a system by virtue of its molecular arrangement and motion of molecules is called **internal energy** or **intrinsic energy** or **microscopic energy**. This energy is associated with thermodynamic state of the system. For perfect gases, internal energy depends only on the temperature of the system as it is assumed that the molecular forces of attraction and repulsion are absent. For non-permanent gas, vapour or liquid, the internal energy strongly depends on temperature and weakly on pressure.

For all gases

$$U = U(T, P)$$

For ideal gases

$$U = U(T)$$

The main characteristics of internal energy are :

- (i) Internal energy is associated with the thermodynamic state of the system. Therefore, it is a point function and a thermodynamic property.
- (ii) Internal energy depends upon the mass of the system, hence it is extensive property.
- (iii) As per Joule's law

$$dV = mC_V dT$$

$$U_2 - U_1 = m \int_{T_1}^{T_2} C_V dT = mC_V (T_2 - T_1) \quad \dots(1.30)$$

For ideal gas

$$C_V = \left(\frac{dU}{dT} \right)$$

- (iv) When a system undergoes a thermodynamic process or change of state both heat and work transfer take place. The net energy transfer is stored within the system and is called **stored energy**

$$\delta Q - \delta W = \delta E \quad \text{or} \quad Q_{1-2} - W_{1-2} = E_2 - E_1$$

The total energy of the system

$$E = \text{P.E.} + \text{K.E.} + U \quad \dots(1.31)$$

For a closed system or non-flow process, when there is no change of P.E. and also there is no flow of mass into or out of the system, there is no kinetic energy present.

$$Q_{1-2} - W_{1-2} = U_2 - U_1$$

- (v) When a closed system undergoes a thermodynamic cycle, the net heat transfer is equal to net work transfer

$$\sum Q_i = \sum W_i \quad \text{or} \quad \oint \delta Q = \oint \delta W$$

The cyclic integral of heat transfer is equal to cyclic integral of work transfer

$$\oint dU = 0$$

- (vi) For an isolated system

$$Q_{1-2} = 0, W_{1-2} = 0$$

$$U_2 = U_1$$

$$\dots(1.34)$$

1.11 FIRST LAW OF THERMODYNAMICS

Heat is a form of energy and energy is conserved.

The idea behind the first law is similar to any thinking person in the modern world. We pay for energy, in the form of electricity, gas, oil etc., which we use for heating, and we know that the amount of heat that we get, is proportional to the amount of energy that we pay for. Heat is said to be generated by doing work on the system. The simplest example is the workdone by a mechanical force : the work is force times the displacement. In simple thermodynamic systems this appears with the force being identified as the pressure (force per unit area) and displacement being identified as the change in volume (displacement of a surface area times that area). Another example of work involves electricity : the force is then identified as the emf (electromotive force) and the displacement as the charge transferred (electric current \times time). Other force-displacement pairs that will appear in this course include surface tension and surface areas, and the chemical potential and chemical concentration.

The first law of thermodynamics is the statement of the principle of conservation of energy. In very general terms, it asserts that the *net flow of energy across the boundary of a system is equal to the change in energy of the system*. For the purpose of thermodynamics it is sufficient to consider only two types of energy flow across a boundary. One of these consists of workdone on or by the system and other is flow of heat either by conduction or by radiation.

Consider quantity dQ of heat supplied to a system. This heat energy is, in general, spent in three ways :

- (i) Partially, it is spent in raising the temperature of the body, which is equivalent of increasing its *internal kinetic energy*.
- (ii) A part of it is spent in doing internal work against molecular attractions which is equivalent of increasing the internal potential energy of the system.
- (iii) The remaining heat energy is spent in expanding the system against external pressure i.e., in doing external work.

If dU_k and dU_p are respectively the change in internal kinetic energy and internal potential energy and dW is the external workdone, then since, "*energy can neither be created nor destroyed but only converted from one form to another*", we have

$$dQ = dU_k + dU_p + dW \quad \dots(1.35)$$

But $dU_k + dU_p = dU =$ increase in total internal energy of the system.

Hence

$$dQ = dU + dW \quad \dots(1.36)$$

Here all quantities are measured in same units (Joule, calories or kilocalories).

Equation (1.36) represents the *differential form of first law of thermodynamics*. This may be stated as,

"In all transformations the heat energy supplied must be balanced by the external workdone plus the increase in internal energy".

The first law of thermodynamics thus establishes an exact relationship between heat and work. The statement of this law involves the assumption that the internal energy is a function of the state of the system (here the term state implies *state of thermodynamic equilibrium*). In fact the system has a definite energy in a definite state. It is obvious that the change in energy $dU (= U_f - U_i)$ depends only on the end (initial and final) states and not at all on the process by which the system is taken from one state to the other. The entire structure of the science of thermodynamics is consistent with this assumption.

From Eq. (1.36), we can make following conclusions :

- (i) As U is a state function, in a cyclic process $\oint dU = 0$

$$\oint dQ = \oint dU + \oint dW = \oint dW \quad \dots(1.37)$$

Therefore, the total work obtained is same as the net heat supplied and no excess work is produced.

- (ii) In a isothermal process, there will be no change in internal energy as at constant temperature, internal energy is constant i.e., $dU = 0$.

$$\text{So } dQ = dW.$$

This means that all the heat supplied to the system is spent to external work.

- (iii) In an adiabatic process, there will be no exchange of heat between the body and the surroundings i.e., $dQ = 0$, so $dW = -dU$.

It means that in an isolated system, work is done by the system at the expense of its own material energy.

1.11.1 Corollaries of the First Law of Thermodynamics

(a) Internal energy of the universe is constant

From the first law of thermodynamics, we have $dU = dQ - dW$. The system absorb dQ heat to perform dW amount of work and at the same time internal energy increases by dU . We now consider that the surroundings, where heat has lost is by an amount dQ and a work dW is done on it.

The change of energy of the surroundings is then written as

$$\Delta U' = dW - \Delta Q$$

$$\Delta U' = -\Delta U$$

$$U + U' = \text{Constant}$$

or

$\dots(1.38)$

Therefore, net change in internal energy of the system and the surroundings taken together would be zero.

(b) Impossibility of the constant motion of the first kind

If work can be done continuously without supply of any heat ($dQ = 0$), then called it is *constant motion of first kind*. When after a series of changes the system returns to its initial state, then the change in internal energy will be zero, i.e.,

$$\oint dU = 0$$

$$\oint dQ = \oint dW$$

...(1.39)

Hence

In a complete cycle, at one stage the working substance receives heat while at other stages it rejects heat. If heat is absorbed, then dQ is positive and if heat is rejected, dQ is negative. So the workdone by the system is taken as positive and the workdone on the system is taken as negative. So from Eq. (1.39), it can be concluded that if after a number of changes the working substance returns to its initial state, then total absorbed heat and total work are same. For that reason, when in cyclic process $\oint dQ = 0$, then $\oint dW = 0$. Hence perpetual motion of first kind is impossible.

1.11.2 Applications of First Law of Thermodynamics

The applications of the first law of thermodynamics to some special processes are as follows:

(a) Isothermal Process (Isothermal Change)

When a change in pressure and volume of a substance takes place but the temperature remains constant, the change (process) is said to be isothermal.

When gas is compressed suddenly some heat is produced but if the compression is slow and the heat produced is removed at once, so that the temperature remains constant, the change is isothermal.

Similarly when a gas is allowed to expand suddenly work is done by the gas and some heat is absorbed. If heat is continuously supplied from outside so that the temperature remains constant, the change is isothermal.

Thus, in an isothermal change the temperature is kept constant by adding heat or taking it away from the substance. As there is no change in temperature, there will be no change in internal energy.

$$dU = 0$$

According to the first law of thermodynamics

$$dQ = dU + dW$$

$$dQ = dW$$

...(1.40)

\therefore In an isothermal process (or process or transformation).

Heat added (or subtracted) = External workdone by (or on) the gas.

For a perfect gas an isothermal change is represented by Boyle's law, given by equation

$$PV = \text{constant.}$$

...(1.41)

(b) Adiabatic Change (Process)

When a change in pressure and volume of a substance taken place but no heat is allowed to enter or leave it, the change (process) is said to be adiabatic.

In an adiabatic change the temperature does not remain constant and no heat from outside is supplied to the system or taken away from it.

It does not mean that the heat of the system remains constant. When a gas is allowed to expand, it does external work and the energy for this purpose is drawn from the heat energy of the gas. The heat energy of the gas, therefore, decreases. When the gas is compressed, work is done on it and the energy gained appears as heat energy. The heat energy of the gas, therefore, increases during an adiabatic process no heat enters or leaves the gas i.e., $dQ=0$.

According to the first law of thermodynamics

$$dQ = dU + dW$$

$$0 = dU + dW$$

$$dU = dW$$

or

\therefore In an adiabatic process,

Increase (or decrease) in internal energy = External workdone on (or by) the gas.

Adiabatic Equation of State

Consider one gm molecule a perfect gas contained in a perfectly non-conducting cylinder fitted with a non-conducting piston as shown in Fig. 1.13. Let the pressure, volume and temperature be P , V and T respectively. Suppose a gas is compressed adiabatically, so that the piston moves inward through a distance dx .

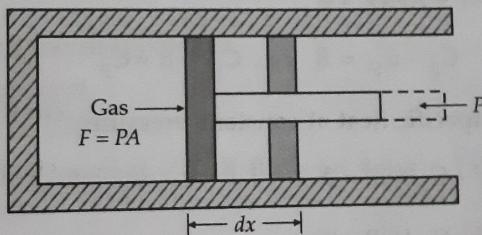


Fig. 1.13 Illustration for adiabatic equation of state.

If A is the area of cross-section of the piston, then total force applied is $P \times A$ and

Workdone by the piston = Force \times Distance

$$= P \times A \times dx$$

$$dW = PdV \quad \dots(1.42)$$

or

as $A dx = dV$ gives the change in volume. The heat generated due to compression causes a rise of temperature dT and is given by $C_V dT$, where C_V is gram molecular specific heat at constant volume.

According to first law of thermodynamics

$$dQ = dU + dW = dU + PdV \quad \dots(1.43)$$

For adiabatic change $dQ=0$

$$dU + PdV = 0$$

Now

$$C_V = \frac{dU}{dt}$$

$$dU = C_V dT$$

...(1.44)

Now putting $dQ=0$ and $dU = C_V dT$ in Eq. (1.43), we have

$$C_V dT + PdV = 0$$

The equation of state for one mole of perfect gas is

$$PV = RT$$

...(1.45)

Differentiating Eq. (1.45), we have

$$PdV + VdP = RdT$$

$$dT = \frac{PdV + VdP}{R}$$

...(1.46)

Substituting the value of dT from Eq. (1.46) in Eq. (1.44), we get

$$C_V \frac{PdV + VdP}{R} + PdV = 0$$

$$\text{or } C_V PdV + C_V VdP + RPdV = 0$$

...(1.47)

$$\text{But } C_P - C_V = R \quad \text{or} \quad C_V + R = C_P$$

where C_P = gram molecular specific heat at constant pressure

$$\text{Here } (C_V + R)PdV + C_V VdP = 0$$

$$\text{or } C_P PdV + C_V VdP = 0$$

...(1.48)

$$\text{Dividing Eq. (1.48) by } C_V PV \text{ and } \frac{C_P}{C_V} = \gamma,$$

where γ = ratio of specific heats at constant pressure and constant volume.

$$\text{Now we have } \gamma \frac{dV}{V} + \frac{dP}{P} = 0$$

...(1.49)

Integrating Eq. (1.49), we have

$$\gamma \log_e V + \log_e P = \text{constant}$$

$$\text{or } \log_e PV^\gamma = \text{constant}$$

$$\text{or } PV^\gamma = \text{constant} = K$$

$$\text{or } PV^\gamma = K$$

...(1.50)

Equation (1.50) is the equation of state for an adiabatic change (process) in terms of thermodynamic variables P and V .

In other words if P_1, V_1 are the initial and P_2, V_2 the final pressure and volume of the gas in adiabatic change, then

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad \dots(1.51)$$

(c) Isobaric process

A thermodynamic process, which takes place at constant pressure is called **isobaric process**.

According to the first law of thermodynamics

$$dQ = dU + dW$$

In an isobaric process, pressure remains constant, so the amount of heat supplied is partly used in doing external work due to increase in temperature. If pressure remains constant at P and increase in volume dV , the external workdone $dW = PdV$.

The shape of curve on $P-V$ diagram for one isobaric process is a straight line parallel to the volume (V) axis for a constant value of pressure (P) as shown in Fig. 1.14.

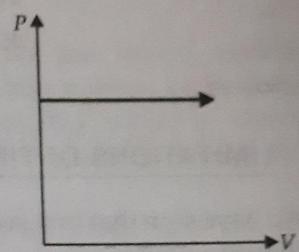


Fig. 1.14 Isobaric process.

(d) Isochoric process

A thermodynamic process in which volume of the system remains constant is known as an **isochoric process**.

According to first law of thermodynamics

$$dQ = dU + dW$$

Since the volume remains constant, $dV = 0$, the workdone $dW = PdV = 0$

$$\therefore dQ = dU \quad \dots(1.52)$$

Thus, whole of the heat supplied to the system is used to increase its internal energy only. Hence the condition that whole of the heat supplied to the system should be used to increase its internal energy only is that the process should be isochoric i.e., takes place at constant volume.

The shape of the curve on a $P-V$ diagram for an isochoric process is straight line parallel to the pressure (P) axis for a constant value of V as shown in Fig. 1.15.

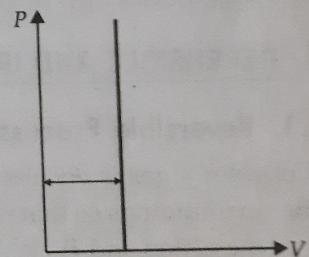


Fig. 1.15 Isochoric process.

Example 1.4 One gram of water (1 cm^3) becomes 1671 cm^3 of steam when boiled at a constant pressure of 1 atm ($1.013 \times 10^5\text{ Pa}$). The heat of vapourization at this pressure is $L_v = 2.256 \times 10^6\text{ J/kg}$, compute (a) the workdone by the water when it vapourizes and (b) its increase in internal energy.

Solution. Given $V_1 = 1\text{ cm}^3 = 10^{-6}\text{ m}^3$, $V_2 = 1671\text{ cm}^3 = 1.671 \times 10^{-3}\text{ m}^3$,

$$P = 1.013 \times 10^5\text{ Pa}, \text{ and } L_v = 2.256 \times 10^6\text{ J/kg.m} = 10^{-3}\text{ kg} = 1\text{ g}$$

(a) The workdone $dW = PdV = P(V_2 - V_1)$
 $= ((1.013 \times 10^5) \times (1671 \times 10^{-6} - 1 \times 10^{-6})) = 169 \text{ J.}$

(b) Increase in internal energy

Heat added to the water to vapourize

$$dQ = mL_v = 10^{-3} \times (2.256 \times 10^6) = 2256 \text{ J}$$

Now from first law of thermodynamics

$$dQ = dU + dW$$

or

$$dU = dQ - dW$$

$$= 2256 - 169 = 2087 \text{ J.}$$

1.12 LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

We have seen that first law of thermodynamics is simply a law of conservation of energy and has following limitations :

- (i) The law considers all forms of energy equivalent i.e., the first law of thermodynamics is law of energy equivalence. This law is necessary condition so far as the account of energy balance is concerned with the possibility of transformation of one kind of energy to another. *it does not tell us the quantity of energy will change from one form to the other.*
- (ii) The first law does not consider the direction of energy transformation.
- (iii) The first law of thermodynamics does not consider the grade of the energy or energy reservoirs. It assumes all energy reservoirs are identical.

1.13 REVERSIBLE AND IRREVERSIBLE PROCESSES

1.13.1 Reversible Processes

Consider a gas is enclosed in a cylinder fitted with a frictionless piston, perfectly insulated from its surroundings so that no heat can leave or enter into it. Some removable weights are placed on top of the piston and P_1, V_1, T_1 are pressure, volume and temperature respectively of the gas in a cylinder at the initial state.

The weights are now removed by very small amount at a time so that the piston moves outward very slowly. The gas is now expanded adiabatically and pressure and volume of the gas adjust themselves so that the system is always in thermodynamic equilibrium. In other words, the adiabatic expansion of the gas is *quasi-static*. The process of removing of weights in small steps is continued so that P_2, V_2, T_2 are pressure, volume and temperature respectively of the gas at the final state.

The weights are now replaced again in very small amount at a time so that the piston moves inwards very slowly. In other words the adiabatic compression of the gas is also *quasi-static*. The process of replacing the weights in small steps is continued till the gas reaches the initial state with P_1, V_1, T_1 as pressure, volume and temperature respectively. During this process of adiabatic compression the gas would pass through exactly the same intermediate steps through which it passed during the adiabatic expansion i.e., all the intermediate states are retraced in the opposite direction. Such a process is known as a *reversible process*.

Hence a reversible process is that which can be retraced in opposite direction, so that the working substance passes through exactly the same condition as it does in the direct process.

In other words it means that in a step where heat is absorbed in the direct process, it is given out in the reverse process and vice versa. Similarly, in a step where work is done by the working substance in the direct process an equal amount of work is done on the working substance in the reverse process.

1.13.2 Conditions of Reversible Process

There are following conditions for reversible process :

- (i) The substance undergoing a reversible change must not lose heat by conduction, convection or radiation or in overcoming friction. No heat must at all be converted into magnetic or electrical energy. Hence for reversibility complete absence of dissipative effects such as friction, electrical resistance, magnetic hysteresis etc., is a must.
- (ii) The change in the pressure and volume of the working substance must take place at an infinitely slow rate, so that when the substance is receiving heat its temperature differs from the hotter body by only an infinitesimal amount and when it is losing heat the temperature again differs by an infinitesimal amount from the colder body. Thus all reversible processes must take place infinitely slowly.

These conditions are never strictly realized in practice because no mechanical process is frictionless and no insulator or conductor is perfect. *Thus rigorous reversibility is an ideal conception while irreversibility is the rule.* However, the conditions necessary for reversibility can be fulfilled approximately and such processes may be regarded as reversible within the limits of experimental errors.

1.13.3 Examples of Reversible Processes

There are following examples of reversible processes :

- (i) If all isothermal and adiabatic changes are performed slowly, then they are reversible. Hence, it is assumed that there is no friction to be overcome as workdone in overcoming friction is wasted in such cases. Since the process is very slow, no energy is wasted in producing oscillations and eddy current and no heat is lost by conduction, convection and radiation. Under these conditions if heat is supplied to a given mass of a gas at constant pressure, it expands and does some external work. If the same amount of work is done on the gas in compressing it, the same quantity of heat will be given out.
- (ii) If the resistance of thermocouple is neglected there will be no heat produced due to Joule's heating effect. In such a case Peltier heating or cooling is reversible. At a junction where a cooling effect results due to Peltier effect when current flows in one direction, an equal heating effect is produced when the current is reversed.
- (iii) Ice melts when a certain amount of heat is absorbed by it. The water so formed can be converted into ice if the same amount of heat is removed from it.
- (iv) Electrolysis process is an example of reversible process.

1.13.4 Irreversible Process

If in any experiment, the weights on the piston are removed quickly, the gas will undergo sudden expansion so that the intermediate states will not be equilibrium state i.e., it will not be possible to define the values of pressure, volume and temperature for these states. Similarly, when the weights are replaced quickly, the gas will undergo sudden compression and the value of pressure, volume and temperature for the intermediate state will again be not defined. Thus during the process of sudden compression it will not be possible to reproduce the intermediate states through which the system passed during sudden expansion. Such a process is known as *irreversible process*.

Hence an irreversible process is that which cannot be retraced in the opposite direction so that the working substance does not pass through the same intermediate states through which it passes during the direct process.

1.13.5 Examples of Irreversible Processes

- (i) Joule-Kelvin effect is irreversible because on reversing the flow of gas, a similar cooling or heating effect is not observed. Similarly diffusion, conduction and radiation are also irreversible.
- (ii) Workdone against friction is irreversible. It is because in reversing the direction of motion again work has to be done against friction.
- (iii) Heat produced by the passage of a current through a resistance is irreversible. It is because even when current is reversed the same effect is observed.
- (iv) Rusting of iron is an example of irreversible process.

1.14 HEAT-ENGINE AND THERMAL EFFICIENCY

We know that mechanical work can be converted into heat and heat into mechanical work. The conversion of heat into work has found various applications in modern civilization. We have considered here the physical principle governing the operation of heat engines, where the same property is applied.

A device, which converts heat into work is called a *heat engine*. Out of various types the most important are reciprocating *steam engines*, *internal combustion engines*, *jet engines* etc. The schematic energy flow diagram for a heat engine is shown in Fig. 1.16. The essential sections of a heat engine are the following :

- (i) **Source/Heat Reservoir.** A hot body, at a fixed high temperature T_1 from which the heat engine can draw heat, is known as source.
- (ii) **Sink/cold Reservoir.** A cold body, at a fixed temperature T_2 , to which any amount of heat can be rejected, is called *sink*.
- (iii) **Working Substance.** The material, which on being supplied with heat, performs mechanical work, is called the *working substance*. In internal-combustion engines, such as those used in automobiles, the working substance is mixture of air and fuel ; in steam turbine it is water.

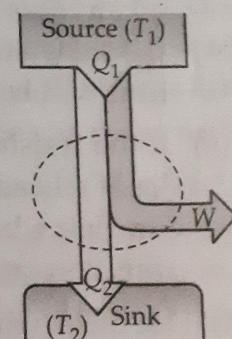


Fig. 1.16 Schematic energy-flow diagram for a heat engine.

There are two types of heat engines :

- (a) *The external combustion engine* where combustion of fuel takes place outside the sink. Steam engine is an example of it.
- (b) *The internal combustion engine* where combustion of fuel takes place inside the sink. Petrol engine, diesel engine etc., are the examples.

In heat engine, the working substance takes in heat from the source converts a part of the external work, gives out the rest to the sink and returns to its initial state. This series of operation constitute a *cycle*. This is shown in Fig. 1.16. The work can be continuously obtained by performing the same cycle again.

The energy transformation of heat engine is shown in Fig. 1.16. The engine itself is represented by the circle. The amount of heat Q_1 supplied to the engine by hot reservoir (source) is proportional to the width of the incoming "pipeline" at the top of the diagram. The width of outgoing pipeline at the bottom is proportional to the magnitude $|Q_2|$ of the heat rejected in the exhaust. The branch line to the right represents the portion of the heat supplied that the engine converts to mechanical work, W .

When an engine repeats the same cycle again and again, Q_1 and Q_2 represent the quantities of heat absorbed and rejected by the engine during *one cycle*; Q_1 is positive and Q_2 is negative.

The net heat Q absorbed per cycle is

$$Q = Q_1 + Q_2 = |Q_1| - |Q_2| \quad \dots(1.53)$$

The useful output of engine is the net workdone W by the working substance.

$$\text{From the first law, } W = Q = Q_1 + Q_2 = |Q_1| - |Q_2| \quad \dots(1.54)$$

Ideally, we would like to convert all the heat Q_1 into work; in that case we would have $Q_1 = W$ and $Q_2 = 0$. Experience shows that this is impossible; there is always some heat wasted, and Q_1 is never zero. We define the thermal efficiency of an engine, denoted by η , as the quotient

$$\eta = \frac{W}{Q_1} \quad \dots(1.55)$$

The thermal efficiency (η) represents the fraction of Q_1 that is converted to work or in other words, we can say that efficiency of an engine is ratio of net workdone by the working substance and heat absorbed by the engine. To put it another way, η is what you get divided by what you pay for. This is always less than unity. In terms of the heat flow diagram of Fig. 1.16, the most efficient engine is one for which the branch pipeline representing the heat thrown away is as narrow as possible.

When we substitute the two expressions for W given by Eq. (1.54) into Eq. (1.55), we get the following equivalent expression for η

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \left| \frac{Q_2}{Q_1} \right| \quad \dots(1.56)$$

NOTE

η is a quotient of two energy quantities, thus is a pure number, without units of course, we must always express W , Q_1 and Q_2 in the same unit.

1.15 CARNOT'S CYCLE

A Carnot cycle is a hypothetical cycle consisting of four distinct processes : two reversible isothermal processes and two reversible adiabatic processes. The cycle was proposed in 1824 by a French Engineer, Sadi Carnot.

The essential elements needed for making an analysis of this cycle are :

- (i) a working substance which is assumed to be perfect gas.
- (ii) two heat reservoirs ; the hot reservoir (heat source) at temperature T_1 and the cold reservoir (heat sink) at temperature T_2 .
- (iii) Piston-cylinder arrangement for getting the work out the working substance. The piston and cylinder walls (excluding the cylinder head) are taken as perfect heat insulators. The cylinder head is imagined to provide alternatively a diathermic cover (perfect heat conductor) and an adiabatic cover (perfect heat insulator).

The piston-cylinder arrangement is shown in Fig. 1.17. There is no friction to the movement of piston inside the cylinder.

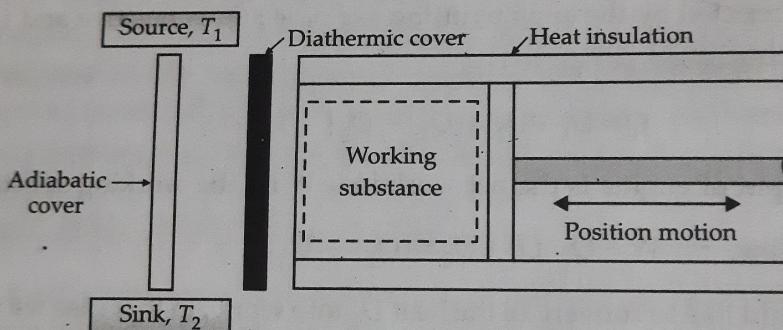


Fig. 1.17 Essential elements for a Carnot cycle.

The sequence of operation for different processes constituting a Carnot's cycle is as shown in Fig. 1.18.

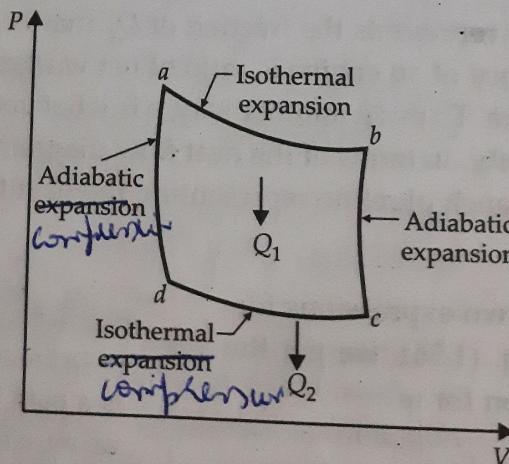


Fig. 1.18 Carnot cycle on P-V plot.

Isothermal Expansion ($a - b$)

The heat is supplied to the working fluid at constant temperature T_1 . This is achieved by bringing the heat source in good thermal contact with the cylinder head through diathermic cover. The gas expands isothermally from the state point $a(P_a, V_a)$ to state point $b(P_b, V_b)$. The heat supplied equals the workdone. Which is represented by area under the curve $a-b$ on pressure-volume plot and is given by

$$Q_1 = W_{a-b} = P_a V_a \log_e \frac{V_b}{V_a} = mRT_1 \log_e \frac{V_b}{V_a}. \quad \dots(1.57)$$

Adiabatic Expansion ($b - c$)

At the end of isothermal expansion (state point b), the heat source is replaced by adiabatic cover. The expansion continues adiabatically and reversibly up to state point $c(P_c, V_c)$. Work is done by the working fluid at the expense of internal energy and its temperature falls to T_2 at state point c .

Isothermal Compression ($c - d$)

After state point c , the piston starts moving inwards and the working fluid is compressed isothermally at temperature T_2 . The constant temperature T_2 is maintained by removing the adiabatic cover and bringing the heat sink in contact with the cylinder heat. The compression continues up to state point d and this position of the piston is so chosen that it lies on the path of reversible adiabatic curve drawn from state point a . The working fluid loses heat to the sink and its amount equals the workdone on the working fluid. The workdone is represented by area under the curve $c-d$ and its amount is given by

$$Q_2 = W_{c-d} = P_c V_c \log_e \frac{V_d}{V_c} = mRT_2 \log_e \frac{V_d}{V_c}. \quad \dots(1.58)$$

Adiabatic Compression ($d - a$)

At the end of isothermal compression (state point d), the heat sink is removed and is replaced by adiabatic cover. The compression now proceeds adiabatically and reversibly till the working fluid returns back to its initial state points a . Work is done on the working fluid, the internal energy increases and temperature is raised to T_1 .

Since all the processes that constitute a Carnot cycle are reversible, the Carnot cycle is referred as a reversible cycle. Further a cyclic heat engine working on the Carnot cycle is called Carnot engine and its thermal efficiency is given by

$$\eta = \frac{\text{Net work output}}{\text{Heat input}} = \frac{W_{net}}{Q_1}$$

There is no heat interaction along the reversible adiabatic processes $b-c$ and $d-a$ and application the first law of thermodynamics for the complete cycle gives,

$$\delta W = \delta Q$$

$$W_{net} = Q_1 - Q_2 = mRT_1 \log_e \frac{V_b}{V_a} - mRT_2 \log_e \frac{V_c}{V_d}$$

$$\eta = \frac{mRT_1 \log_e \frac{V_b}{V_a} - mRT_2 \log_e \frac{V_c}{V_d}}{mRT_1 \log_e \frac{V_b}{V_a}}$$

$$= 1 - \frac{T_2}{T_1} \times \frac{\log_e \frac{V_c}{V_d}}{\log_e \frac{V_b}{V_a}}$$

For the adiabatic expansion processes (b - c) and (d - a)

$$\frac{T_b}{T_c} = \left(\frac{V_c}{V_d} \right)^{\gamma-1} \quad \text{and} \quad \left(\frac{T_a}{T_d} \right) = \left(\frac{V_d}{V_a} \right)^{\gamma-1}$$

Since $T_b = T_a = T_1$ and $T_c = T_d = T_2$, the above expression gives

$$\frac{T_1}{T_2} = \left(\frac{V_c}{V_b} \right)^{\gamma-1} = \left(\frac{V_d}{V_a} \right)^{\gamma-1}$$

or

$$\frac{V_c}{V_b} = \frac{V_d}{V_a}$$

or

$$\frac{V_c}{V_d} = \frac{V_b}{V_a}$$

Substituting the above relation in Eq. (1.59), we get

$$\eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1} \quad \dots(1.60)$$

Following conclusions can be drawn from the efficiency of a Carnot engine :

- The efficiency is independent of the working substance and depends upon the temperatures of source and sink.
- If $T_2 = 0$, the engine will have an efficiency of 100%. However, that means absence of heat sink which is violation of Kelvin-Planck statement of the second law of thermodynamics.
- The efficiency is directly proportional to temperature difference $(T_1 - T_2)$ between the source and the sink.
- Higher the temperature difference between source and sink, the higher will be the efficiency obtained.

- (v) The efficiency increases with an increase in temperature of source and a decrease in temperature of sink.
- (vi) If $T_1 = T_2$, no work will be done and efficiency will be zero.

Metallurgical considerations and the high cost of temperature resisting materials limits the high temperature T_1 . The lower temperature T_2 is limited by atmosphere or sink conditions.

1.15.1 Carnot's Cycle is Impracticable

Carnot cycle gives the maximum possible thermal efficiency which can be obtained for the given temperature limits. The Carnot's engine, however, is a hypothetical device and it is not possible devise due to the following reasons :

- (i) All the four processes have to be reversible. This necessitates that the working fluids have no internal friction between the fluid particles and no mechanical friction between the piston and cylinder walls.
- (ii) The heat absorption and rejection have to take place with infinitesimal temperature differences. Accordingly, the rate of energy transfer will be very low and the engine will deliver only infinitesimal power.
- (iii) For attaining isothermal operation, the piston movement is required to be very slow. However, the piston must move fast for the adiabatic process. A variation in the speed of the piston during different processes of a cycle is rather impossible.
- (iv) There is insignificant difference in the slopes of isothermal and adiabatic lines. Consequently the $P-V$ plot is greatly extended both in the horizontal and vertical directions. The cylinder then involves greater pressures and volumes, and as such becomes bulky and heavy.

This hypothetical device, however, serves as a yardstick or standard of perfection against which the performance of any practical heat engine can be compared.

Example 1.5 What is the highest possible theoretical efficiency of a heat engine operating with a heat reservoir of furnace gases at $2100^\circ C$, when the cooling water available is at $15^\circ C$?

Solution. Given :

$$\text{Temperature of furnace, } T_1 = 2100 + 273 = 2373 \text{ K and}$$

$$\text{Temperature of cooling water, } T_2 = 15 + 273 = 288 \text{ K}$$

$$\text{Now, } \eta = 1 - \frac{T_2}{T_1} = 1 - \frac{288}{2373} = 0.878 \text{ or } 87.8\%.$$

Example 1.6 The efficiency of a Carnot cycle is $1/6$. On reducing the temperature of the sink by $60^\circ C$, the efficiency increases to $1/3$. Find the initial and final temperatures between which the cycle is working.

Solution. Let T_1 and T_2 be the initial Kelvin temperature of the source and sink respectively. Then the efficiency is given by

$$\eta = 1 - \frac{T_2}{T_1} = \frac{1}{6} \quad \dots(i)$$

When T_2 is decreased to $T_2 - 60^\circ\text{C}$ ($1^\circ\text{C} = 1\text{K}$ in size). The new efficiency is

$$\eta' = 1 - \frac{T_2 - 60}{T_1} = \frac{1}{3}$$

From Eqs. (i) and (ii), we have

$$\frac{T_2}{T_1} = 1 - \frac{1}{6} = \frac{5}{6}$$

and

$$\frac{T_2 - 60}{T_1} = 1 - \frac{1}{3} = \frac{2}{3}$$

Dividing Eq. (iii) by Eq. (iv), we get

and

$$\frac{T_2}{T_2 - 60} = \frac{5}{6}$$

Solving, we get

$$T_2 = 300\text{ K} = 27^\circ\text{C}$$

Putting the value of T_2 (in Kelvin) in Eq. (i), we get

$$\frac{300}{T_1} = \frac{1}{6}$$

This gives

$$T_1 = 360\text{ K} = 87^\circ\text{C}$$

The cycle is initially working between 87°C and 27°C . Finally, the temperature of sink is reduced 60°C , so that the cycle works between 87°C and -33°C .

1.16 CARNOT'S ENGINE AND CARNOT'S REFRIGERATOR

Any heat engine operating in a Carnot cycle is called a *Carnot's engine* and may be represented schematically as shown in Fig. 1.19.

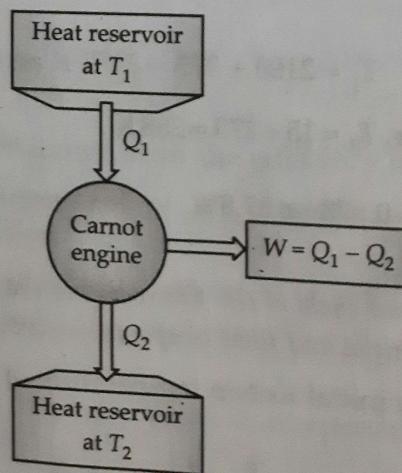


Fig. 1.19 A Carnot's engine.