

# First Law of Thermodynamics

Energy can be in two forms: (a) energy in *transit*, like heat and work transfer observed at the boundaries of a system, and (b) energy in *storage*, where energy is stored either *macroscopically* by virtue of motion, position or configuration of the system, or *microscopically* in the molecules or atoms constituting the system.

## 4.1 First Law for a Closed System Undergoing a Cycle

The transfer of heat and the performance of work may both cause the same effect in a system. Heat and work are different forms of the same entity, called energy, which is conserved. Energy which enters a system as heat may leave the system as work, or energy which enters the system as work may leave as heat.

Let us consider a closed system which consists of a known mass of water contained in an adiabatic vessel having a thermometer and a paddle wheel, as shown in Fig. 4.1. Let a certain amount of work  $W_{1-2}$  be done upon the system by the paddle wheel. The quantity of work can be measured by the fall of weight which drives the paddle wheel through a pulley. The system was initially at temperature  $t_1$ , the same as that of atmosphere, and after work transfer let the temperature rise to  $t_2$ . The pressure is always 1 atm. The process 1-2 undergone by the system is shown in Fig. 4.2 in generalized thermodynamic coordinates  $X$ ,  $Y$ . Let the insulation now be removed. The system and the surroundings interact by heat transfer till the system returns to the original temperature  $t_1$ , attaining the condition of thermal equilibrium with the atmosphere. The amount of heat transfer  $Q_{2-1}$  from the system during this process, 2-1, shown in Fig. 4.2, can be estimated. The system thus executes a cycle, which consists of a definite amount of work input  $W_{1-2}$  to the system followed by the transfer of an amount of heat  $Q_{2-1}$  from the system. It has been found that this  $W_{1-2}$  is always proportional to the heat  $Q_{2-1}$ , and the constant of proportionality is called the Joule's equivalent

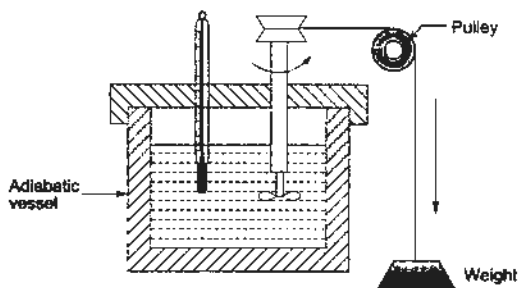


Fig. 4.1 Adiabatic work

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

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

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

$$\oint dW = J \oint dQ$$

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

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

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

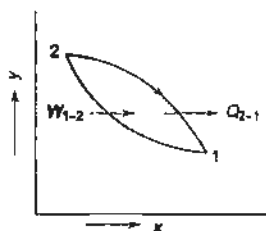


Fig. 4.2 Cycle completed by a system with two energy interactions: adiabatic work transfer  $W_{1-2}$  followed by heat transfer  $Q_{2-1}$

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

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

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

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

$$\text{Therefore} \quad Q - W = \Delta E$$

where  $\Delta E$  is the increase in the energy of the system

$$\text{or} \quad Q = \Delta E + W \quad (4.2)$$

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

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

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

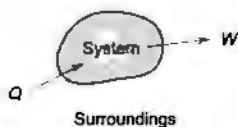


Fig. 4.3 Heat and work interactions of a system with its surroundings in a process

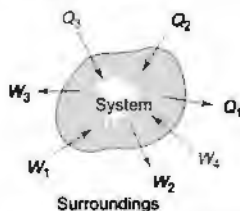


Fig. 4.4 System-surroundings interaction in a process involving many energy fluxes

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

### 4.3 Energy—A Property of the System

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

$$Q_A = \Delta E_A + W_A \quad (4.3)$$

and for path  $B$

$$Q_B = \Delta E_B + W_B \quad (4.4)$$

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

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

or

$$W_A + W_B = Q_A + Q_B$$

or

$$Q_A - W_A = W_B - Q_B \quad (4.5)$$

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

$$\Delta E_A = -\Delta E_B \quad (4.6)$$

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

$$\Delta E_A = -\Delta E_C \quad (4.7)$$

From equations (4.6) and (4.7)

$$\Delta E_B = \Delta E_C \quad (4.8)$$

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

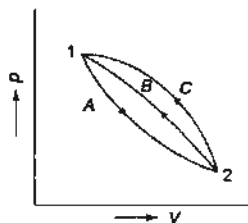


Fig. 4.5 Energy—a property of a system