The First Law of Thermodynamics

The recognition of heat and internal energy as forms of energy makes possible a generalization of the law of conservation of mechanical energy to include heat and internal energy in addition to work and external potential and kinetic energy. Indeed, the generalization can be extended to still other forms, such as surface energy, electrical energy, and magnetic energy. This generalization was at first a postulate. However, the overwhelming evidence accumulated over time has elevated it to the stature of a law of nature, known as the first law of thermodynamics. One formal statement is:

Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms.

In application of the first law to a given process, the sphere of influence of the process is divided into two parts, the system and its surroundings. The region in which the process occurs is set apart as the system; everything with which the system interacts is the surroundings. The system may be of any size depending on the application, and its boundaries may be real or imaginary, rigid or flexible. Frequently a system consists of a single substance; in other cases it may be complex. In any event, the equations of thermodynamics are written with reference to some well-defined system. This focuses attention on the particular process of interest and on the equipment and material directly involved in the process. However, the first law applies to the system and surroundings, and not to the system alone. In its most basic form, the first law requires:

$$\Delta(Energy\ of\ the\ system) + \Delta(Energy\ of\ surroundings) = 0$$

Where the difference operator "Δ" signifies finite changes in the quantities enclosed in parentheses. The system may change in its internal energy, in its potential or kinetic energy, and in the potential or kinetic energy of its finite parts. Since attention is focused on the system, the nature of energy changes in the surroundings is not of interest. In the thermodynamic sense, heat and work refer to energy in transit across the boundary which divides the system from its surroundings. These forms of energy are not stored, and are never contained in a body or system. Energy is stored in its potential, kinetic, and internal forms;

these reside with material objects and exist because of the position, configuration, and motion of matter.

Internal energy

The sum of all the microscopic forms of energy is called the **internal energy** of a system and is denoted by **U.** The **microscopic** forms of energy are those related to the molecular structure of a system and the degree of the molecular activity, and they are independent of outside reference frames.

Kinetic energy

The energy that a system possesses as a result of its motion relative to some reference frame is called *kinetic energy (KE).* When all parts of a system move with the same velocity, the kinetic energy is expressed as

$$KE = m\,\frac{V^2}{2} \qquad kJ$$

or, on a unit mass basis,

$$KE = \frac{V^2}{2} \qquad kJ/kg$$

where *V* denotes the velocity of the system

potential energy

The energy that a system possesses as a result of its elevation in a gravitational field is called **potential energy** (*PE*) and is expressed as:

$$PE = mgz \qquad kJ$$

or, on a unit mass basis,

$$PE = gz \qquad kJ/kg$$

where g is the gravitational acceleration and z is the elevation.

Energy Change of a System, ΔE_{system}

The determination of the energy change of a system during a process involves the evaluation of the energy of the system at the beginning and at the end of the process, and taking their difference. That is:

Energy change = Energy at final state - Energy at initial state

energy can exist in numerous forms such as internal (*sensible, latent, chemical, and nuclear), kinetic, potential, electric, and magnetic, and their sum constitutes the total energy E of a system.* In the absence of *electric, magnetic*, and *surface tension* effects (i.e., for simple compressible systems), the change in the total energy of a system during a process is the sum of the changes in its internal, kinetic, and potential energies and can be expressed as:

$$\Delta E_{system} = \Delta U + \Delta KE + \Delta PE \qquad (1)$$

$$\Delta U = m(u_2 - u_1)$$

$$\Delta KE = \frac{1}{2} m (v_2^2 - v_2^2)$$

$$\Delta PE = mg (z_2 - z_1)$$

for **stationary systems,** the changes in kinetic and potential energies are zero (that is, $\Delta KE = \Delta PE = 0$), and the total energy change relation in Eq. (1) reduces to $\Delta E = \Delta U$ for such systems.

Stationary Systems

$$z_1 = z_2 \rightarrow \Delta PE = 0$$
$$V_1 = V_2 \rightarrow \Delta KE = 0$$
$$\Delta E = \Delta U$$

For Closed System (non – flow system)

In thermodynamics, a closed system can exchange energy (as heat or work), but not matter, with its surroundings.

Δ(energy of the system) + Δ(energy of the surrounding) = 0

$\Delta U + \Delta K_E + \Delta P_E = Q\text{-}W$

If ΔK_E and ΔP_E are negligible

$\boxed{\Delta U = Q\text{-}W}$ …(2) First law of thermodynamics for closed system

For Open System (flow System)

In open systems Fig (4), matter may flow in and out of the system boundaries. The first law of thermodynamics for open systems states: the increase in the internal energy of a system is equal to the amount of energy added to the system by matter flowing in and by heating, minus the amount lost by matter flowing out and in the form of work done by the system.
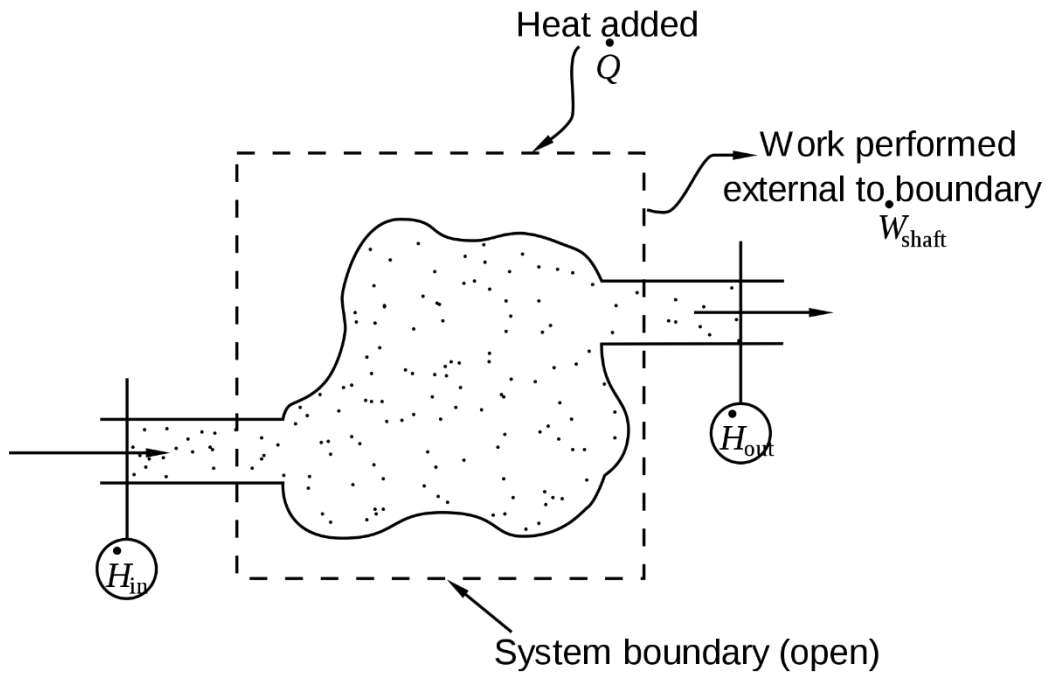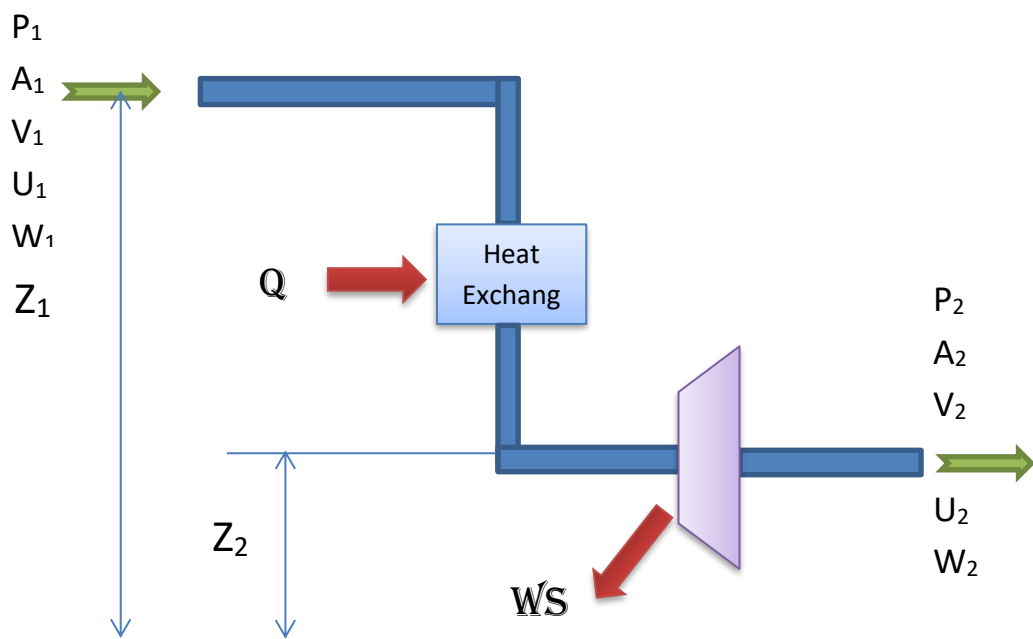
Fig. (4): Mass and heat cross the boundaries of a open system.

Consider the following unit of open system :

Basis $= 1$ kg unit mass

Starting with

$$\Delta U + \Delta K_E + \Delta P_E = Q - W \qquad \dots (1)$$

$$\Delta K_E + \frac{1}{2}V_2^2 - \frac{1}{2}V_1^2 = \frac{1}{2}\Delta V^2$$

$$\Delta P_E = z_2 g + z_1 g = g(z_2 - z_1) = g\Delta z$$

Then eq. (1) becomes..

$$\Delta U + \Delta \frac{\Delta V^2}{2} + g\Delta z = Q - W \qquad \dots (3)$$

$$W = W_1 + W_2 + W_S$$

$$W_1 = P_1 A_1 \times \frac{V_1}{A_1} = P_1 V_1$$

$$W_2 = P_2 A_2 \times \frac{V_2}{A_2} = P_2 V_2$$

$$\therefore W = P_1 V_1 + P_2 V_2 + W_S$$

$$\therefore \Delta U + \frac{\Delta V^2}{2} + g\Delta z = Q - (P_1 V_1 - P_2 V_2 - W_S)$$

$$\Delta U + \frac{\Delta V^2}{2} + g\Delta z = Q - W_S - (P_1 V_1 - P_2 V_2)$$

$$\Delta U + \Delta PV + \frac{\Delta V^2}{2} + g\Delta z = Q - W_S$$

When: $\Delta U + \Delta PV = \Delta H$

$$\Delta H + \frac{\Delta V^2}{2} + g\Delta z = Q - W_S \qquad \dots (4)$$

If ΔV and Δz are Negligible then…

$$\Delta H = Q - W_S \qquad\qquad \text{.... (5)}$$

(for first law for open steady state system).

The steady state process means:

1- The conditions at all points in the apparatus are constant with time.

2- Mass flow rate to the system equal to mass transfer out of the system.

3- Rate of work or heat transfer must be constant.

Energy Balance for Closed Systems

If the boundary of a system does not permit the transfer of matter between the system and its surroundings, the system is said to be closed, and its mass is necessarily constant. The development of basic concepts in thermodynamics is facilitated by a careful examination of closed systems, and for this reason they are treated in detail in the following sections.

Far more important for industrial practice are processes in which matter crosses the system boundary as streams that enter and leave process equipment. Such systems are said to be open, once the necessary foundation material has been presented. Since no streams enter or leave a closed system, no internal energy is transported across the boundary of the system. All energy exchange between a closed system and its surroundings then appears as heat and work, and the total energy change of the surroundings equals the net energy transferred to or from it as heat and work. The second term of Eq. (1.1) may therefore be replaced by

$$\Delta(Energy\ of\ surroundings) = \pm Q \pm W$$

The choice of signs used with Q and W depends on which direction of transport is regarded as positive. Heat Q and work W always refer to the system, and the modern sign convention makes the numerical values of both quantities positive for transfer into the system from the surroundings.The corresponding quantities taken with reference to the surroundings, Q_{surr} and W_{surr} have the opposite sign,i.e., $Q_{surr}= -Q$ and $W_{surr}= -W$. With this understanding:

$$\Delta(Energy\ of\ surroundings) = Qsurr + wsurr = -Q - w \qquad \text{Equation (1.1)}$$

now become:

$$\Delta \,(Energy\ of\ the\ system) \;=\; Q \,+\, W$$

This equation means that the total energy change of a closed system equals the net energy transferred into it as heat and work.

Closed systems often undergo processes that cause no change in the system other than in its internal energy. For such processes, Eq. (2.2) reduces to:

$$\boxed{\Delta U^t = Q + W}$$

where U_t: is the total internal energy of the system. Equation (2.3) applies to processes involving finite changes in the internal energy of the system. For diffrential changes:

$$\boxed{dU^t = dQ + dW}$$

Both of these equations apply to closed systems which undergo changes in internal energy only. The system may be of any size, and the values of Q, W, and U^t are for the entire system, which must of course be clearly defined.

All terms in Eqs. (2.3) and (2.4) require expression in the same units. In the SI system the energy unit is the joule. Other energy units in use are the m kgf, the calorie, the (ft lb$_f$), and the (Btu).

For a closed system of (n) moles Eqs . may now be written:

$$\boxed{\Delta(nU) = n\,\Delta U = Q + W} \tag{2.5}$$

$$\boxed{d(nU) = n\,dU = dQ + dW} \tag{2.6}$$

In this form, these equations show explicitly the amount of substance comprising the system.

The equations of thermodynamics are often written for a representative unit amount material, either a unit mass or a mole. Thus for n = 1 Eqs. (2.5) and (2.6) become:

$$\Delta U \;=\; Q \,+\, W \ and \ dU \;=\; dQ \,+\, dW$$

The basis for Q and W is always implied by the quantity appearing on the left side of the energy equation.

Equilibrium

Equilibrium is a word denoting a static condition, the absence of change. In thermodynamics it means not only the absence of change but the absence of any tendency toward change on a macroscopic scale. Thus a system at equilibrium exists under conditions such that no change in state can occur. Since any tendency toward change is caused by a driving force of one kind or another, the absence of such a tendency indicates also the absence of any driving force. Hence for a system at equilibrium all forces are in exact balance. Whether a change actually occurs in a system not at equilibrium depends on resistance as well as on driving force. Many systems undergo no measurable change even under the influence of large driving forces, because the resistance to change is very large.

Different kinds of driving forces tend to bring about different kinds of change. For example, imbalance of mechanical forces such as pressure on a piston tend to cause energy transfer as work; temperature differences tend to cause the flow of heat; gradients in chemical potential tend to cause substances to be transferred from one phase to another. At equilibrium all such forces are in balance.

In many applications of thermodynamics, chemical reactions are of no concern. Forexample, a mixture of hydrogen and oxygen at ordinary conditions is not in chemical equilibrium, because of the large driving force for the formation of water. However, if chemical reaction is not initiated, this system can exist in long-term thermal and mechanical equilibrium, and purely physical processes may be analyzed without regard to possible chemical reaction. This is an example of the fact that systems existing at partial equilibrium are often amenable to thermodynamic analysis.

Example

Water flows over waterfall 100 m in height. Take 1 kg of the water as the system, and assume that it does not exchange energy with the surrounding.

a) what is the potential energy of the water in the top of the falls with respect of the base of the falls?

b) what is the kinetic energy of the water just before it strikes bottom?

c) after 1 kg of the water enters the revir below the falls, what change has occurred in it state?

Solution

The 1 kg of water exchange no energy with surrounding therefore

$$\Delta E_{sys} = 0$$

Since the system process energy in internal, kainetic and potential forms

$$\Delta U + \Delta E_k + \Delta E_p = 0$$

This equation applies to each port of process

a) $E_P = mzg = 1kg \times 100\ m \times 9.8066\ m\ s^{-1}$

$$= 980.66\ \frac{kg\ m^2}{s^2} = 980.66\ N.m = 980.66\ J$$

b) during the free fall of water no mechanism exist for conversion of potential or kinetic energy into internal energy, thus ΔU must be zero

$$\Delta E_k + \Delta E_P = E_{k2} - E_{k1} + E_{P2} - E_{P1} = 0$$

As on excellent approximation let $E_{k1} = E_{P2} = 0$ then

$$E_{k2} = E_{P1} = 980.66\ J$$

c) the 1kg of water strikes bottom and mixes with other falling water to form a river, the resulting turbulence has the effect of converting kinetic energy into internal energy. During this process ΔE_P is essensially zero

$$\Delta U + \Delta E_k = 0 \qquad or \qquad \Delta E_k = E_{k2} - E_{k3}$$

However, the river velocity is assumed small making E_{k3} negligible, thus.

$$\Delta U = E_{k2} = 980.66\ J$$