

## First Law of Thermodynamics

### **Energy and work in thermodynamics:**

Thermodynamics is concerned with energy relationships involving heat, mechanical energy, and other aspects of energy and energy transfer. A thermodynamic system is one that can interact with its surroundings in at least two ways, one of which must be transfer of heat; also it is possible to do the mechanical work.

In mechanics the work done is defined as

$$dW = Fdx \dots\dots\dots (1)$$

where  $W$  = work done,  $F$  = force, and  $dx$  = distance.

In gaseous system we are more concerned with pressure rather than force, and since the pressure is defined as force per unit area, i.e.

$$P = \frac{F}{A}$$

$$\Rightarrow F = PA$$

Thus eq (1) can be written as

$$dW = PAdx \quad [ \because dV = Adx ]$$
$$\Rightarrow dW = PdV$$

In a definite change of volume from  $V_1$  to  $V_2$

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

If the pressure is constant, then

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

This expression for work done at constant pressure is widely used in thermodynamics.

### **Internal energy and first law:**

The transfer of heat and performance of work constitute two means of adding energy to or subtracting energy from a system. Once the transfer of energy has occurred, the system is said to have undergone a change in internal energy.

To introduce the concept of internal energy and to relate it with the heat and work we can consider a system undergoes a change from state 1 to state 2 along a definite path. We can compute the heat  $Q$  absorbed by the system and work  $W$  done by it. We can repeat the procedure for different paths and list them. We found that for different path the work done and heat absorbed (or liberated) is also different. It means that the work done and heat absorbed (or liberated) do not depend only on the initial and final state but also on the path of the process. We, now again compute the quantity  $Q - W$  for each and every different path and surprisingly found that this particular quantity remains same for every time, whatever the path is. Therefore, from the result, we can conclude, although  $Q$  and  $W$  individually depend upon the path, but there is a quantity  $Q - W$  which depends only upon the initial and final state and not upon the path. We call the quantity  $Q - W$ , the change in internal energy of the system since  $Q$  comes from transfer of heat and  $W$  comes from performance of work, and their difference is, in fact, the transfer in energy. Therefore,

$$U_1 - U_2 = \Delta U = Q - W$$

This expression is known as first law of thermodynamics. In language, we can state the first law as, "There exists a state variable in a thermodynamic system which is independent of the path of the process and depends only upon the initial and final state and which is equal to the transfer in energy."

**Application of first law:**

We can apply first law for different systems.

**a) Cyclic process:** If a system is carried through a process that eventually returns to its initial state then the process is called cyclic process.

For this process the initial and final internal energy remains unchanged since the system returns to the initial state, i.e.

$$U_2 = U_1$$

$$\therefore \Delta U = U_2 - U_1 = 0 = Q - W$$

Thus, for cyclic process  $Q = W$

**b) Isolated system:** A system in which no heat enters or leaves and no work is performed on or by the system is known as isolated system, i.e. for isolated system

$$Q = 0, W = 0$$

$$\therefore \Delta U = U_2 - U_1 = Q - W = 0$$

Therefore, for isolated system  $Q = W$

**c) Adiabatic system:** A system in which no heat enters or leaves the system is known as adiabatic system, i.e. for adiabatic process

$$Q = 0$$

$$\therefore \Delta U = Q - W = 0 - W = -W$$

The negative work means that the work done on the system and the system is compressed. In that case, the internal energy of the system increases. On the other hand the positive work is the work done by the system, the system expands and internal energy decreases in this case.

**d) Isochoric system:** A process taking place at constant volume is known as isochoric process. For this case

$$W = PdV = P \times 0 = 0$$

$$\therefore \Delta U = U_2 - U_1 = Q - W = Q$$

Therefore, for isochoric process  $\Delta U = Q$

Positive heat represents that heat enters the system and negative heat is the liberated heat.

**e) Isothermal process:** A process taking place at constant temperature is said to be isothermal process. In general, none of the quantities  $Q$ ,  $W$ , or  $U_2 - U_1$  is zero. There are a few special cases in which the internal energy of a system depends only on temperature, not on pressure or volume. An ideal gas and an ideal paramagnetic crystal are two examples. When such a system undergoes an isothermal process, its internal energy does not change, and therefore  $Q = W$ . This relation does not hold for systems other than those mentioned.

**f) Isobaric process:** A process taking place at constant pressure is called an isobaric process. For isobaric process the work done is

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

We can consider a special case of boiling water. The liquid water become water vapour at a particular point known as boiling point in which the pressure and temperature is constant. In this case

$$W = P(V_V - V_L), \quad \text{where } V_V = \text{volume of vapour} \ \& \ V_L = \text{volume of water}$$

The heat required for this case is

$$Q = mL, \quad \text{where } L = \text{heat of vaporization} \ \& \ m = \text{mass of the water}$$

Thus, the first law becomes for boiling process

$$\therefore \Delta U = U_V - U_L = Q - W = mL - P(V_V - V_L)$$

**Differential form of first law:**

We know that the first law of thermodynamics is

$$\Delta U = U_1 - U_2 = Q - W$$

This expression of first law is in the finite form referring to a process in which states 1 and 2 differ in pressure, volume, and temperature by a finite amount. Now, let us suppose that states 1 and 2 differ only infinitesimally. Then a small amount of heat  $dQ$  is transferred, a small amount of work  $dW$  is done, and the corresponding small internal energy changes is  $dU$ . In this case the first law becomes

$$dU = dQ - dW$$

In systems such as we have been considering, the work is given by  $dW = PdV$ , and the first law becomes

$$dQ = dU + PdV$$

This form is called the differential form of first law.

**Example 1:** An ideal gas is kept at constant temperature  $T$  and undergoes an isothermal expansion in which its volume changes from  $V_1$  to  $V_2$ . How much work is done?

**Solution:**

We know, the work done is

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

For an ideal gas

$$PV = nRT$$

$$\therefore P = \frac{nRT}{V}$$

Thus, work done becomes

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

$$\Rightarrow W = nRT \int_{V_1}^{V_2} \frac{dV}{V} \text{ [Since, } n, R, \text{ and } T \text{ are constant]}$$

$$\therefore W = nRT \ln \frac{V_2}{V_1}$$

This expression is the work done in an isothermal system. In an expansion,  $V_2 > V_1$  and  $W$  is positive.

Again, at constant  $T$

$$P_1V_1 = P_2V_2$$

$$\therefore \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

Therefore, the isothermal work may be expressed also in the form

$$W = nRT \ln \frac{P_1}{P_2}$$

**Problem for practice:** Exercise 18- 4, 18- 12, 18- 14, 18- 15, 18- 16(a) (c), etc.