

## LECTURE 9

### FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is the thermodynamic expression of **the conservation of energy**.

This law most simply stated by saying that “energy can not be created or destroyed” or that “the energy of the universe is constant”.

This law can be stated for a system (control mass) undergoing a cycle or for a change of state of a system.

Stated for a system undergoing a cycle, the cyclic integral of the work is proportional to the cyclic integral of the heat.

Mathematically stated, for a control mass undergoing a cyclic process such as in Joule’s experiment and for consistent set of units

$$\int dQ_{\text{from system}} = \int dW_{\text{on system}}$$

$$\text{or } \int dQ_{\text{from system}} - \int dW_{\text{on system}} = 0$$

The important thing to remember is that the first law states that the energy is conserved always.

**Sign convention** The work done by a system on the surroundings is treated as a positive quantity.

Similarly, energy transfer as heat to the system from the surroundings is assigned a positive sign. With the sign convention one can write,

$$\int dQ = \int dW$$

**Consequences of the first law:** Suppose a system is taken from state 1 to state 2 by the path 1-a-2 and is restored to the initial state by the path 2-b-1, then the system has undergone a cyclic process 1-a-2-b-1. If the system is restored to the initial state by path 2-c-1, then the system has undergone the cyclic change 1-a-2-c-1. Let us apply the first law of thermodynamics to the cyclic processes 1-a-2-b-1 and 1-a-2-c-1 to obtain

$$\int_{1-a-2} dQ + \int_{2-b-1} dQ - \int_{1-a-2} dW - \int_{2-b-1} dW = 0$$

$$\int_{1-a-2} dQ + \int_{2-c-1} dQ - \int_{1-a-2} dW - \int_{2-c-1} dW = 0$$

Subtracting, we get

$$\int_{2b1} dQ - \int_{2c1} dQ - (\int_{2b1} dW - \int_{2c1} dW) = 0$$

We know that the work is a path function and hence the term in the bracket is non-zero. Hence we find

$$\int_{2b1} dQ = \int_{2c1} dQ$$

That is heat is also a path function.

**Energy is a property of the system:** By rearranging we can have

$$\int_{2b1} (dQ - dW) = \int_{2c1} (dQ - dW)$$

It shows that the integral is the same for the paths 2-b-1 and 2-c-1, connecting the states 2 and 1. That is, the quantity  $\int (dQ - dW)$  does not depend on the path followed by a system, but

depends only on the initial and the final states of the system. That is  $\int (dQ - dW)$  is an exact differential of a property. This property is called energy (E). It is given by

$$dE = dQ - dW$$
$$E = KE + PE + U$$

where U is the internal energy. Therefore,

$$dE = d(KE) + d(PE) + dU = dQ - dW$$

Quite often in many situations the KE or PE changes are negligible.

$$dU = dQ - dW$$

An isolated system does not exchange energy with the surroundings in the form of work as well as heat. Hence  $dQ = 0$  and  $dW = 0$ . Then the first law of thermodynamics reduces to  $dE = 0$  or  $E_2 = E_1$  that is energy of an isolated system remains constant.

### **Perpetual Motion Machine of the first kind:**

An imaginary device which delivers work continuously without absorbing energy from the surroundings is called a Perpetual Motion machine of the first kind. Since the device has to deliver work continuously, it has to operate on a

cycle. If such a device does not absorb energy from its surroundings  $\int dQ = 0$ . From the first law, it can be observed that  $\int dW = 0$ , if  $\int dQ = 0$ . Therefore such a device is impossible from first law of thermodynamics.

**First law analysis of non-flow processes:** The first law of thermodynamics can be applied to a system to evaluate the changes in its energy when it undergoes a change of state while interacting with its surroundings. The processes that are usually encountered in thermodynamic analysis of systems can be identified as any one or a combination of the following elementary processes:

- Constant volume (isochoric) process
- Constant pressure (isobaric) process
- Constant temperature (isothermal) process.
- Adiabatic process.

Constant volume process: Suppose a gas enclosed in a rigid vessel is interacting with the surroundings and absorbs energy  $Q$  as heat. Since the vessel is rigid, the work done  $W$  due to

expansion or compression is zero. Applying the first law, we get

$$dU = dQ \text{ or } Q = U_2 - U_1$$

That is, heat interaction is equal to the change in internal energy of the gas. If the system contains a mass  $m$  equal of an ideal gas, then

$$Q = \Delta U = mC_v (T_2 - T_1)$$

The path followed by the gas is shown on a P-V diagram. Now consider the fluid contained in a rigid vessel as shown. The vessel is rigid and insulated. Shaft work is done on the system by a paddle wheel as shown in Fig. a. In Fig. b electric work is done on the system. Since the vessel is rigid, the PdV work is zero. Moreover, the vessel is insulated and hence  $dQ = 0$ . Application of the first law of thermodynamics gives

$$dU = dQ - dW = dQ - (dW_{pdv} + dW_s)$$

$$\text{or } dU = -dW_s \text{ or } -W_s = \Delta U = U_2 - U_1$$

Where  $dW_{pdv}$  is the compression /expansion work and  $dW_s$  is the shaft work. That is increase in internal energy of a system at a constant volume, which is enclosed by an adiabatic wall, is equal to the shaft work done on the system.

**Constant pressure process:** Several industrial processes are carried out at constant pressure. A few examples of constant pressure processes are: (a) reversible heating/cooling of a gas (b) phase change (c) paddle wheel work (d) electrical work. For a constant pressure process, the work done  $W$  is given by

$$W = \int PdV = P (V_2 - V_1)$$

Application of the first law of thermodynamics gives

$$dU = dQ - dW = dQ - PdV = dQ - d(PV)$$

$$\text{or } dQ = dU + d(PV) = d(U + PV) = dH$$

$$\text{or } Q = \Delta H$$

That is in a constant pressure process, the heat interaction is equal to the increase in the enthalpy of the system. Now consider the constant pressure processes in which the system is enclosed by an adiabatic boundary. Application of the first law gives:

$$dU = dQ - dW = dQ - (PdV + dW_s)$$

Here, the net work done ( $dW$ ) consists of two parts – the  $PdV$  work associated with the motion of the boundary and  $(-dW_s)$ , the shaft work (or electrical work) done by the surroundings. Since the system is enclosed by an adiabatic boundary,  $dQ = 0$  the equation can be written as

$$-dW_s = dU + d(PV) = dH$$

That is, the increase in the enthalpy of the system is equal to the shaft work done on the system.

**Constant temperature process:** Suppose a gas enclosed in the piston cylinder assembly is allowed to expand from  $P_1$  to  $P_2$  while the temperature is held constant. Then application of the first law gives:

$$dU = dQ - dW = dQ - PdV$$

It is not possible to calculate work and heat interactions unless the relationships between the thermodynamic properties of the gas are known. Suppose the gas under consideration is an ideal gas (which follows the relation  $Pv = RT$  and  $u = u(T)$  only) then for an isothermal process,

$$dU = 0$$



$$dQ = PdV = RTdv/v \text{ or } Q = W = RT\ln(v_2/v_1)$$

**Reversible adiabatic (Isentropic process):**