Lecture Notes Dated: Aug 18, 2012

Work: Work done by and on the System

Work in thermodynamics always represents an exchange of energy between a system and its surroundings. As in mechanics, the work is defined as

$$W = \int Fdl$$

or,
$$\delta W = Fdl$$

where δW represents a differential quantity of work.

We adopt the usual sign convention, that the value of δW is ***negative when work is done on the system and positive when work is done by the system***.

In thermodynamics one can finds work done by a force distributed over an area, i.e., by a pressure p acting through a volume V, as in case of a fluid pressure exerted on a piston. Thus, if p is an external pressure exerted on a system causing a change of dV in volume,

$$\delta W = pdV \qquad (01)$$

For a finite change in volume, the pressure will change and the work done is

$$W = \int pdV \qquad (02)$$

The SI unit of work and energy is therefore the *newton-meter*, which is called a *Joule*.

Dependence of Work on Path

The work done by or on the system depends not only on the initial and final states but also on the intermediate states, i.e., on the path of the process. For example, consider a system (Figure 2) that is taken from an initial equilibrium state i to a final equilibrium state f by two different paths a and b as shown in the indicator diagram. The areas iaf and ibf are different and hence the work done in taking the system from i to state f will be different for differente paths. Thus, work is not the property of the system. Thus, ***δW is an inexact differential*** and integration of δW can not be expressed as the difference between two quantities that depends entirely on the initial and final states. Thus, ***work is a path function***.

Figure 2 *The pV diagram*

Heat

In thermodynamics heat, like work, is regarded as *energy in transit* across the boundary separating two systems or a system from its surroundings. However, quite unlike work, heat transfer, a non-mechanical energy transfer, results due to temperature difference between two systems or a system and surroundings, and simple contact is the only requirement for heat to be transferred by conduction. Therefore, *heat is that which is transferred between a system and its surroundings by virtue of a temperature difference only*.

If a system loses energy by any other methods, it is said to do work. Thus, work is the transfer of energy without a temperature difference.

The sign convention used for a quantity of heat is opposite to that used for work. *Heat added to a system is given by a positive number, whereas heat taken from a system is given by a negative number*. The SI units of heat are those of work and energy, i.e., *newton-meter* or *Joule*.

Dependence of Heat on Path

When a system changes from an initial state 1 to final state 2, the amount of heat transferred depends not only on the initial and final states but also on the intermediate states, i.e., on the path of the process. The heat flown into the system will be different for different paths. It depends how the system is heated. Thus, ***δQ is an inexact differential***, i.e., heat is not the property of the system and integration of δQ can not be expressed as the difference between two quantities which depend only on the initial and final states. Thus, ***heat is also a path function***.

Internal Energy: As a State Function

We know that matter is made up of a large number of atoms or molecules. At temperature above absolute zero, they are in a state of constant motion and hence each one of them has kinetic energy. The sum of kinetic energies of all molecules is known as internal kinetic energy. Also, due to inter-atomic/ inter-molecular interactions, each atom/ molecule making up the system possesses potential energy. The total energy stored in the system due to interactions is called total internal potential energy. *The sum of total internal kinetic and potential energies of all molecules constitute the* ***internal energy*** *of the system*. We denote it by the symbol U. We are usually interested only in the changes in the value of internal energy dU, which may be occurred due to the following three types of interactions:

1. Thermal Interaction, i.e., by exchanging heat with a system.
2. Mechanical Interaction, i.e., work being done on or by a system.
3. Diffusive Interaction, i.e., exchanging matter with a system.

The internal energy of the system is in all cases by assumption, a single-valued ***function of the variables of state***. Because internal energy is a function of state, i.e., its differential dU is exact and can be expressed as the algebraic sum of two inexact differential. Thus the internal energy function is independent of path.