LECTURE 3

Internal Energy

- The molecule as a whole can move in x, y and z directions with respective components of velocities and hence possesses kinetic energy.
- There can be rotation of molecule about its center of mass and than the kinetic energy associated with rotation is called rotational energy.
- In addition the bond length undergoes change and the energy associated with it is called vibrational energy.
- The electron move around the nucleus and they possess a certain energy that is called electron energy.
- The microscopic modes of energy are due to the internal structure of the matter and hence sum of all microscopic modes of energy is called the internal energy.

Bulk kinetic energy (KE) and potential energy (PE) are considered separately and the other energy of control mass as a single property (U).

The total energy possessed by the body is given by:

$$E = KE + PE + U$$

Work

Whenever a system interacts with its surroundings, it can exchange energy in two ways- work and heat.

In mechanics, work is defined as the product of the force and the displacement in the direction of the force.

Work done when a spring is compressed or extended: According to Hooke's law

$$\text{Spring force} = - k (x - x_0)$$

Where k is the spring constant, x_0 is the equilibrium position, and x is the final position. The negative sign shows that the direction of the spring force is opposite the direction of the displacement from x_0. The external force is

equal in magnitude but opposite in sign to the spring force, so

External force (force of your hands) = $k (x - x_0)$.

Now, we want to calculate the work done when we stretch the spring from position 1 to position 2.

$$W = \int F\,dx = \int k (x - x_0)\, d(x-x_0) = 1/2\, k [(x_2-x_0)^2 - (x_1-x_0)^2]$$

Work done when a volume is increased or decreased

Consider a gas in a container with a movable piston on top. If the gas expands, the piston moves out and work is done by the system on the surroundings.

Alternatively, if the gas inside contracts, the piston moves in and work is done by the surroundings on the system. Why would the gas inside contract or expand?

It would if the external pressure, P_{ex}, and the internal pressure, P_{in}, were different. To calculate the work done in moving the piston,

we know that the force = pressure times area and then work equals pressure times area times distance or work equals pressure times the change in volume. So, W = the integral of (P_{ex}) dV

The differential work done (dW) associated with a differential displacement (dl) is given by

$$dW = F\ dl$$

For a piston cylinder assembly,

$$dW = F\ dl = PA\ (dl) = P\ dV$$

If the gas is allowed to expand reversibly from the initial pressure P to final pressure P, then the work done is given by

$$W = \int p\ dV$$

- The integral represents the area under the curve on a pressure versus volume diagram. Therefore the work depends on the path followed and work is a path function and hence not a property of the system.

- The above expression does not represent work in the case of an irreversible process.

- The thermodynamic definition of work is " Work is said to be done by a system on the surrounding if the sole effect external to the system could be reduced to the raising of a mass through a distance".

Heat

Heat like work, is a form of energy.

The energy transfer between a system and its surroundings is called heat if it occurs by virtue of the temperature difference across the boundary.

The two modes of energy transfer – work and heat- depend on the choice of the system.

Heat energy moves from a hotter body to a colder body upon contact of the two bodies.

If two bodies at different temperatures are allowed to remain in contact, the system of two bodies will eventually reach a thermal equilibrium (they will have the same temperature).

A body never contains heat. Rather heat is a transient phenomenon and can be identified as it crosses the boundary.