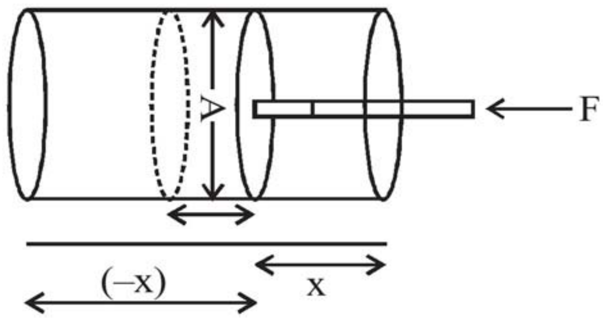
PRESSURE-VOLUME WORK

This category of work takes place when a shift in volume is prompted by the impact of an external pressure.

Let's contemplate a scenario involving a cylinder with a cross-sectional area denoted as A, equipped with a piston characterized by its lack of friction. Within this cylinder, there's a confinement of n moles of an ideal gas. In this setup, an external force F is applied to drive the piston inward, which leads to a specific displacement dx in the piston's position. This type of work is precisely the outcome of changes in volume occurring under the influence of external pressure within this system.



small change in volume of gas (dV) = A. dx

Small work done dw = F. dx

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

$F = PA$

$dW = PA. dx$

⇒ $dV = -A. dx$

(-ive sign indicates work is done by the system i.e., gas is expanding against P_{ext})

⇒ $dW = -P_{ext.}\, dV$

⇒ $W = -\int P_{extremal}\, dV$

Sign Convention

Work done by the system is –ive.

Work done on the system is +ive

- During expansion dV is +ive and hence sign of w is -ive i.e., work is done by the system and hence Expansion Work is always negative.

During compression, dV is -ive which gives +ive value of w i.e., work is done on the system and hence Compression work is always positive.

Internal Energy (U Or E)

Let's consider a system with a mass 'M' that is in motion within a gravitational field at a velocity 'v.' In the Earth's frame of reference, the total energy of this system can be expressed as the sum of three components: E = K + V + U Here,

(K represents the kinetic energy, V stands for potential energy, U signifies internal energy.)

Typically, when investigating thermodynamic systems, they are treated as being at rest, which implies that the kinetic energy (K) is equal to zero. Additionally, when the impact of gravitational fields or other external fields is disregarded, we are left with a simplified equation: E = U.

In simpler terms, in the absence of external fields that might contribute potential energy, and when the system is at a state of rest with no external kinetic energy, the total energy is referred to as the internal energy of the system.

The concept of internal energy within a gas confined in a container is defined concerning a coordinate system that is anchored to the container itself. When examined at a microscopic or atomic scale, internal energy can manifest in various forms, including:

The system's energy encompasses a combination of various components, including:

- The kinetic energy associated with the motion of the molecules within the system.
- The potential energy linked to the constituents of the system.
  For instance, in the case of a crystal composed of dipolar molecules, the potential energy will undergo changes when an electric field is applied to the system.
- The internal energy that is stored in the form of molecular vibrations and rotations.
- The internal energy stored in the form of chemical bonds, which can be released through a chemical reaction.

The collective sum of these diverse energy forms associated with the system is typically denoted by the symbol 'U' and is recognized as the internal energy of the system. This internal energy, represented as 'U,' encompasses the cumulative impacts of these varied energy components within the system under examination.

$$U = U_{translational} + U_{rotational} + U_{vibrational} + U_{intermolecular} + U_{electronic} + U_{relativistic}$$

Among these components, $U_{relativistic}$ and $U_{electronic}$ remain unaffected by standard heating processes. Essentially, the kinetic energy terms and $U_{intermolar}$ contribute to the heat supplied to the system. Consequently, the heat capacity of a sample is contingent on these four terms.

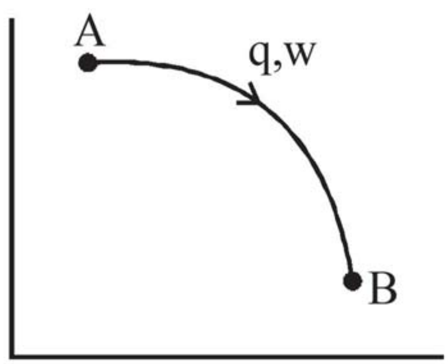
In the case of an ideal gas, $U_{intermolecular}$ equals zero due to the absence of intermolecular forces of attraction. However, $U_{intermolecular}$ possesses a substantial and negative value in solids and liquids.

For an ideal gas U is only function of temperature e.g. $U = F(T) + \text{Constant}$

Because ideal gas internal energy lacks pressure or volume terms, the internal energy (U) of an ideal gas remains unaffected by changes in pressure and volume.

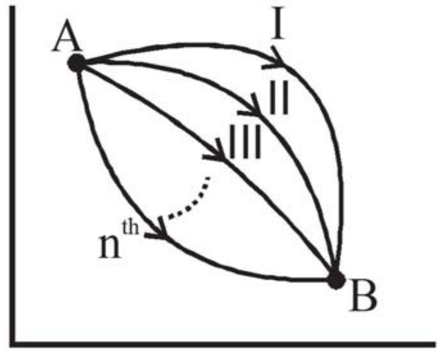
- Internal Energy is an extensive Property and is a state function.

If a system is present in particular thermodynamic state say 'A' it has fixed amount of internal energy U_A. Suppose by a process the system is taken from state A to state B then.



$$\Delta U = U_B - U_A$$

Since U is state function. This implies between any two fixed states, there can be infinite process or path, but ΔU in all process will remain the same. (Property of a function of state) Consider a system taken from state A to B by n^{th} different paths.



i.e., $\Delta U_1 = \Delta U_2 = \Delta U_3$ ....

For a given system, Internal Energy can be represented as a function of volume and temperature U = f (T, V) and the overall change in I.E., can be calculated mathematically as:

$$dU = \left(\frac{\partial U}{\partial T}\right)_v . dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

- For isochoric process: $dV = 0$

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT$$

$$dU = Cv. dT$$

Overall change in I.E. $\Delta U = \int C_v.dT$

- For an ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$dU = C_V. dT$$

$$\Delta U = \int C_v. dT$$

For a real gas $\left(\frac{\partial U}{\partial V}\right)_T$ is Positive when attractive forces dominate (in both compression & expansion) and $\left(\frac{\partial U}{\partial V}\right)_T$ is Negative when repulsive forces dominate (in both compression & expansion).

Note: that heat and work involve in all the process are different but ΔU is same. This mean heat and work are indefinite quantities while ΔU is a definite quantity.