

## Chemical Thermodynamics - I

### BASICS

### Section - 1

#### Internal Energy :

When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the **internal energy**,  $U$  of the system, which may change, when

- heat passes into or out of the system,
- work is done on or by the system,
- matter enters or leaves the system.

Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as :  $\Delta U = q + w$  ... (I)

For a given change in state,  $q$  and  $w$  can vary depending on how the change is carried out. However,  $q + w = \Delta U$  will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (**isolated system**) i.e., if  $w = 0$  and  $q = 0$ , then  $\Delta U = 0$ .

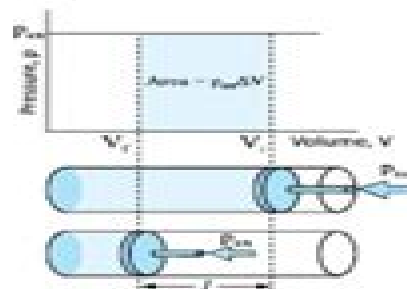
The equation,  $\Delta U = q + w$  is mathematical statement of the first law of thermodynamics, which states that *the energy of an isolated system is constant*.

Many chemical reactions involve the generation of gases capable of doing mechanical work or the generation of heat. It is important for us to quantify these changes and relate them to the changes in the internal energy. Let us see how!

#### Pressure-Volume work :

For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is  $V_i$  and pressure of the gas inside is  $p$ . If external pressure is  $p_{ex}$  which is greater than  $p$ , piston is moved inward till the pressure inside becomes equal to  $p_{ex}$ . Let this change be achieved in a single step and the final volume be  $V_f$ .

During this compression, suppose piston moves a distance,  $l$ . **Figure :** Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure,  $p_{ex}$  (in single step) is equal to the shaded area.



We also know,  $\text{pressure} = \frac{\text{force}}{\text{area}}$  Therefore,  $\text{force on the piston} = p_{ex} \cdot A$

If  $w$  is the work done on the system by movement of the piston then

$$w = \text{force} \times \text{distance} = p_{ex} \cdot A \cdot l = p_{ex} \cdot (-\Delta V) = -p_{ex} \Delta V = -p_{ex} (V_f - V_i) \quad \dots (II)$$

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**R. Kinsky**



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