

### Concept to remember:

Chemical Thermodynamics-II:

Internal Energy: Total energy possessed by a system, this includes all kinds of energy a system may possess.

Internal energy may change:

- i) Heat comes into or out of the system
- ii) Work is done on or by the system
- iii) Matter enters or leaves the system

### Sign Convention:

Work done on the system: + (positive)

Work done by the system: - (negative)

Heat added to the system: + (positive)

Heat extracted from system: - (negative)

First law of Thermodynamics:  $\Delta U = q + w$  ... This is law of energy conversion

Work done on a gas:  $W = -\int_{V_i}^{V_f} P_{ex} dV$

$P_{ex}$  is external pressure and expressed as  $P_{in} \pm dp$  and  $P_{in}$  is pressure of the gas. As  $dp$  is very small, we can write  $W = -\int_{V_i}^{V_f} P_{in} dV$

For  $n$  mol ideal gas  $P_{in} = P$ ,  $P = nRT/V$ ; so,  $W = -\int_{V_i}^{V_f} (nRT/V) dV = -nRT \ln \frac{V_f}{V_i}$

Free expansion: expansion in vacuum,  $P_{ex} = 0$