

Work done during Isothermal Reversible Process $\Rightarrow$

$$W = - \int_{V_1}^{V_2} P_{\text{ext}} dV$$

$$P_{\text{ext}} = P_{\text{int}} \pm dp$$

$$W = - \int_{V_1}^{V_2} (P_{\text{int}} \pm dp) dV$$

$$W = - \int_{V_1}^{V_2} P_{\text{int}} dV \pm \int_{V_1}^{V_2} dp dV \rightarrow 0$$

$$W = - \int_{V_1}^{V_2} P_{\text{int}} dV$$

for an ideal gas, $PV = nRT$

$$P_{\text{int}} = \frac{nRT}{V}$$

$$W = - \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$W = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$W = -nRT \ln V \Big|_{V_1}^{V_2}$$

$$W = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$W = -2.303 nRT \log \left(\frac{V_2}{V_1} \right)$$

$$(\because \ln(x) = 2.303 \log(x))$$

for a real gas

$$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

$$W = - \int_{V_1}^{V_2} \left[\frac{nRT}{V-nb} - \frac{n^2a}{V^2} \right] dV$$

$$W = -nRT \ln \left(\frac{V_2-nb}{V_1-nb} \right) - n^2a \left[\frac{1}{V_2} - \frac{1}{V_1} \right]$$

For irreversible process $\Rightarrow$

$$W = -P_{\text{ext}} dV$$

$$W = -P_{\text{ext}} (V_2 - V_1)$$

$$PV = nRT \Rightarrow V = \frac{nRT}{P}$$

$$W = -P_2 (V_2 - V_1) \quad (\because P_{\text{ext}} = P_2)$$

$$W = -P_2 \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$$

$$W = -nRT \left(1 - \frac{P_2}{P_1} \right)$$

State function and path function $\Rightarrow$ If a function depends only on the state of the system and not on the path by which the state has been attained are called state function.

Ex. Enthalpy (H), Internal energy (U) etc.

If the function depends on the path as, process then it is called path function.

Ex. Heat (Q), work (W). ~~etc.~~

- * State function are exact differential but path function are not.
- * The integral of exact differential over a cycle path is zero.

$$\oint U = 0.$$

Internal Energy $\Rightarrow$ The energy possessed by a system by virtue of the motion of atoms and molecules. It is a state function and denoted by ' U '.

First law of thermodynamics $\Rightarrow$ The total energy of the universe is constant.

If a system is in state 1, has internal energy U_1 and 'q' amount of heat is given to the system. The system does 'w' amount of work and its internal energy becomes U_2 , then

according to the first law of thermodynamics

$$U_1 + q = U_2 + (-W)$$

$$U_2 - U_1 = q + W$$

$$\boxed{\Delta U = q + W} \Rightarrow \text{mathematical form of first law of thermodynamics}$$

- again $W = -P dV$

$$\Delta U = q - P dV$$

$$dU = dq + dw$$

$$\boxed{dU = dq - P dV}$$