

Enthalpy : \rightarrow

When a system shows no mechanical energy, but is still capable of doing work, it is said to possess internal energy or intrinsic energy.

In an infinitesimal reversible process, change in this internal energy is given by

$$dU = dQ - dW \quad (\because \text{from the first law})$$

$$dQ = Tds \quad (\because \text{from the second law})$$

$$\therefore dU = Tds - pdv \quad (dW = pdv)$$

Therefore, when entropy remains constant, $dU = -pdv$
($\because ds = 0$ at constant entropy)

$$\therefore p = - \left(\frac{\partial U}{\partial v} \right)_s$$

$$\text{Similarly } T = \left(\frac{\partial U}{\partial s} \right)_v$$

Thus the derivative of gravitational potential or other potentials gives intensity of the corresponding field, the basic coordinates p and T are given by derivatives of the internal energy. This is why internal energy is considered as the first thermodynamic potential. At constant volume $dv = 0$ and, therefore,

$$dU = Tds = dQ$$

$$\text{But, } C_v = \frac{dQ}{dT} \text{ at const. volume}$$

$$= \frac{dU}{dT} \text{ at constant volume}$$

$$\therefore C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

Combining U with the products ' pV ' and ' TS ' which are

of the dimensions of energy, other auxiliary state functions may be introduced. Besides U , three more state functions or properties of particular significance are defined as

$$\text{Enthalpy (H)} = U + pV$$

$$\text{Helmholtz free energy (F)} = U - TS$$

$$\text{Gibbs free energy (G)} = H - TS$$

$$\text{or, } U + pV - TS$$

Enthalpy and its significance: \rightarrow By defn we have

$$H = U + pV$$

$$\therefore dH = dU + pdv + vdp$$

$$= (Tds - pdv) + pdv + vdp \quad (\because dU = Tds - pdv)$$

$$dH = Tds + vdp$$

$$\therefore T = \left(\frac{\delta H}{\delta s} \right) \quad \text{and} \quad V = \left(\frac{\delta H}{\delta p} \right)$$

Thus T and V are given by derivatives of H . This justifies its selection as the second thermodynamic potential. The significance of this potential is that it gives a similar formula for C_p as we have for C_v , we have

$$C_v = \left(\frac{\delta U}{\delta T} \right)_v$$

At constant pressure,

$$dH = Tds \quad (\because dp = 0)$$

$$\therefore dH = da$$

But $C_p = \frac{da}{dT}$ at const. pressure = $\frac{dH}{dT}$ at const. pressure

$$\text{or, } C_p = \left(\frac{\delta H}{\delta T} \right)_p$$

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