

①

{ B.Sc Part I Physics (Hons) }
 { Dr Satyadeo Narayan Singh }
 S.B. college, Ara

Ques: Define Helmholtz function (or potential) of system and justify its name. Explain its importance?

Ans: We have $F = U - TS$
 $dF = dU - Tds - SdT$
 $= Tds - pdv - Tds - SdT$
 $= -pdv - SdT$

At constant temperature $dT=0$ and so on

$$\therefore P = - \left(\frac{dF}{dv} \right)_T$$

$$\text{Similarly } S = - \left(\frac{dF}{dT} \right)_V$$

Thus P and S are given by derivatives of A . This justifies its selection as the third thermodynamic potential. Its significance is revealed when we consider reversible isothermal process.

$$dU = Tds - dw = d(Ts) - dw \quad (T = \text{const})$$

$$\Rightarrow d(U - Ts) = -dw$$

$$\therefore dF = -dw \quad (\because F = U - Ts \text{ by definition})$$

Here dw is the work done by the system and $-dw$ is the work done on the system. Thus the significance of free energy is that its decrease represents mechanical work available from it in a 'reversible isothermal process'. This is the reason why Helmholtz termed it free energy of the system.

Another significance is revealed when we consider reversible ^{isochoric} isothermal process. In such process $dw = pdv = 0$

Since $dv=0$ at constant volume, Hence in such a process

$$dF = 0 \text{ or } A = \text{constant}$$

Thus in a reversible ~~isothermal~~ isothermal-isochoric processes, free energy of the system remain constant