

Qu.: Thermodynamic Potentials:

Ans. A conservative mechanical system is in equilibrium when the potential energy is minimum. The functions U, H, A and G are called thermodynamic potentials because their minimum values determine equilibrium states of a thermodynamics system under various constraints. However, The term is commonly applied to A and G only.

A = Helmholtz free energy is called thermodynamic potential at constant volume and

G = Gibb's free energy is called thermodynamic potential at constant pressure.

The thermodynamic functions P, V, T and S can be expressed in terms of the partial derivatives of U, H, A, and G. with two independent variables.

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

(1)

In Eq.(1), each function has a different pair of variables as its characteristic independent variables.

$$U = U(S,V), H = H(S,P), A = A(T,V), G = G(T,P) \quad (2)$$

Since they are functions of state it follows that

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \quad (3)$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T, \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad (4)$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S, \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \quad (5)$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \quad \left(\frac{\partial G}{\partial P}\right)_T = V \quad (6)$$

If any one of the functions U, H, F, G is known explicitly in terms of its characteristic variables, then we have complete information on the system. We may also calculate any of the other parameters of the system from differentiation of that one potential. The equation expressing the thermodynamic potential

in terms of its characteristic variables is then known as the characteristic equation of the system. **The internal energy is obtained from the definition of A.**

$$\begin{aligned}
 U &= A + T S \\
 &= A - T \left(\frac{\partial A}{\partial T} \right)_V
 \end{aligned} \tag{7}$$

Now, we first evaluate the term $\left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right)$. Now,

$$\begin{aligned}
 \left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right) &= \frac{1}{T} \left(\frac{\partial A}{\partial T} \right) - \frac{A}{T^2} \\
 -T^2 \left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right) &= -T \left(\frac{\partial A}{\partial T} \right) + A
 \end{aligned} \tag{8}$$

i.e.

$$U = A - T \left(\frac{\partial A}{\partial T} \right)_V = -T^2 \left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right)$$

or

$$U = -T^2 \left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right) \tag{9}$$

Similarly

$$\begin{aligned}
 H &= U + PV \\
 &= A - T \left(\frac{\partial A}{\partial T} \right)_V - V \left(\frac{\partial A}{\partial V} \right)_T
 \end{aligned} \tag{10}$$

And

$$\begin{aligned}
 G &= A + PV \\
 &= A - V \left(\frac{\partial A}{\partial V} \right)_T \\
 G &= -V^2 \left(\frac{\partial}{\partial V} \right)_T \left(\frac{A}{V} \right)
 \end{aligned} \tag{11}$$

Similarly, if G is known as a function of T and P, then Eq.(10) give us the entropy S and volume V. Therefore

$$\begin{aligned}
 H &= G + TS \\
 &= G - T \left(\frac{\partial G}{\partial T} \right)_P \\
 H &= -T^2 \left(\frac{\partial}{\partial T} \right)_P \left(\frac{G}{T} \right)
 \end{aligned} \tag{12}$$

and

$$\begin{aligned}
 U &= H - PV \\
 &= G - T \left(\frac{\partial G}{\partial T} \right)_P - P \left(\frac{\partial G}{\partial P} \right)_T
 \end{aligned} \tag{13}$$

And

$$\begin{aligned}
 A &= G - PV \\
 &= G - P \left(\frac{\partial G}{\partial P} \right)_T
 \end{aligned} \tag{14}$$

Eq.(9) to Eq.(14) is known as the Gibb's-Helmholtz relations. The differences in U and A also true for isothermal process at constant volume, the H and G in an isothermal isobaric process. Thus for internal energy

$$(U_f - U_i) = (A_f - A_i) - T \left[\left(\frac{\partial A_f}{\partial T} \right)_V - \left(\frac{\partial A_i}{\partial T} \right)_V \right] \tag{15}$$

$$(\Delta U) = (\Delta A) - T \left[\left(\frac{\partial(\Delta A)}{\partial T} \right)_V \right] \tag{16}$$

$$\Delta H = \Delta G - T \frac{\partial}{\partial T} (\Delta G)_P \tag{17}$$

The specific heat capacity C_V and C_P can also expressed in terms of second order derivatives of A and G.

$$C_V = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_V \tag{18}$$

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p \quad (19)$$
