

THERMODYNAMIC POTENTIALS AND MAXWELL'S RELATIONS:

A mechanical system is said to be in a state of equilibrium when the potential energy of the system is minimum. Similarly, in thermodynamics, internal energy (U), Helmholtz Free Energy (F), Enthalpy (H), and Gibbs Free Energy (G) is similar to potential energy in mechanics. To achieve thermodynamic equilibrium, the direction of thermodynamical processes must be in such a direction as to minimize the respective thermodynamical function (potential). Four functions U, F, H and G are called thermodynamic potentials and all have the dimensions of energy.

The four thermodynamic potentials are:

Internal Energy: $U = TS - PV$

Enthalpy: $H = U + PV$

Helmholtz Free Energy: $F = U - TS$

Gibbs Free Energy: $G = H - TS = U - TS + PV$

Four potentials $U(S,V)$, $F(T,V)$, $H(S,P)$ and $G(P,T)$ are functions of thermodynamic variables S, T, P and V.

1. Thermodynamic Potential U(S,V) and The First Maxwell's Equation:

Since $dU = TdS - PdV$

Taking partial differentials of U w.r.t. S and V, we have

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P$$

Since dU is an exact differential.

We get

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

This is the First Maxwell's Equation

2. Thermodynamic potential F(T,V) and The second Maxwell's Equation:

The Helmholtz Free Energy (F) defined by

$$F = U - TS$$

On differentiating

$$dF = - PdV - SdT$$

Taking partial differentials of F w.r.t. T and V, we have

$$\left(\frac{\partial F}{\partial T}\right)_V = -S$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -P$$

Since dF is perfect differential

we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

This is the second Maxwell's Equation.

3. Thermodynamic potential H(S,P) and The third Maxwell's Equation:

Enthalpy (H) is given by

$$H = U + PV$$

On differentiating

$$dH = TdS + VdP$$

Taking partial differentials of H w.r.t. S and P, we have

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

Since dH is perfect differential

We get

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

This is the third Maxwell's Equation.

4. Thermodynamic potential G(P,T) and The fourth Maxwell's

Equation:

The Gibbs function is defined as;

$$G = H - TS$$

Differentiating we get

$$dG = VdP - SdT$$

Taking partial differentials of G w.r.t. P and T, we have

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

Since dH is perfect differential

We get

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

This is the fourth Maxwell's Equation.