

Maxwell's Relation and Thermodynamic Potential

2. Different Types of Thermodynamic Potential and Maxwell Relation

Thermodynamic potentials are different form of energy which can be used in different thermodynamic process. Thermodynamic potentials are path independent variables so they are perfect differential.

If F is unique thermodynamic potential defined by variables x and y as $F = F(x, y)$ and if it is perfect differential then $dF = Mdx + Ndy$

Where $M = \left(\frac{\partial F}{\partial x}\right)_y$ and $N = \left(\frac{\partial F}{\partial y}\right)_x$ then M and N will satisfy the condition

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Internal Energy: U and second from the first laws of thermodynamics

$$dU = TdS - PdV$$

from Legendre transformation

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \quad \text{from given relation one can derive Maxwell}$$

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

Enthalpy: (H) the enthalpy is defined as $H = U + PV$

$$dH = dU + PdV + VdP$$

from Laws of thermodynamics

$$TdS = dU + PdV$$

$$dH = TdS + VdP$$

from Legendre transformation

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

The Enthalpy H is Extensive quantity, which can not be measured directly. Thus change in enthalpy is more useful.

ΔH is positive in endothermic reaction and negative in exothermic reaction.

From above relation one can derive Maxwell relation $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

ΔH of a system is equal to sum of non-mechanical work done on it and the heat supplied to it.

Helmholtz Free Energy: (F) the Helmholtz free energy is defined $F = U - TS$

$$dF = dU - TdS - SdT$$

From laws of thermodynamics $dU = TdS - PdV$

$$dF = TdS - PdV - TdS - SdT$$

$$dF = -PdV - SdT$$

From Legendre transformation

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

From above relation one can derive Maxwell relation $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

The free Energy F, which is available energy for work in reversible isothermal process.

Gibbs Energy: 'G' is defined as $G = H - TS$.

$$G = U + PV - TS$$

$$dG = dU + PdV - VdP - TdS - SdT$$

$$TdS - PdV + PdV + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

from Legendre transformation

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

From above relation one can derive Maxwell relation $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

Gibbs free energy is popularly as free enthalpy.

The Gibbs free energy is Maximum amount of nonexpanding work that can be exacted from a closed system.

The maximum will activated when the system is in reversible process.

Gibbs free energy is also treated as chemical potential.

In thermodynamics, chemical potential, as partial molar free energy, is a form of potential energy that can be absorbed or relived during a chemical reaction.

The chemical potential of a species in the minute can be defined the slope of the energy at system with respect to a change in the no of moles.

$$\mu = \left.\frac{dG}{dN}\right|_V$$

where μ is chemical potential, G is Gibbs energy and N is no of molecules

Example: Prove that internal energy U is given by

$$(a) U = \left(\frac{\partial(F/T)}{\partial(1/T)}\right)_V$$

$$(b) H = \left[\frac{\partial(G/T)}{\partial(1/T)}\right]_P$$

Solution: (a) $F = U - TS = U + TS$

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

$$U = F + T\left(\frac{-\partial F}{\partial T}\right)_V = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial(F/T)}{\partial T}\right)_V = \left(\frac{\partial(F/T)}{\partial(1/T)}\right)_V$$

Solution: (b) $H = \left[\frac{\partial(G/T)}{\partial(1/T)}\right]_P$

$$G = H - TS$$

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

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P = -T^2\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_P\right) = \left[\frac{\partial(G/T)}{\partial(1/T)}\right]_P$$