

S. S. College. Jehanabad (Magadh University)

Department : Physics

Subject : Quantum Mechanics

Class : B.Sc(H) Physics Part III

Topic: Thermodynamic Potentials

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Thermodynamic Potentials

We can also derive Maxwell's Relations using Thermodynamical relations .

The state of a system can be completely described by any two of the five variables, P , V , T , S , and U . Out of these, U the internal energy is determined by using the remaining four, as shown below :

According to first law of thermodynamics,

$$\delta Q = dU + PdV$$

And from the second law of thermodynamics,

$$\delta Q = TdS$$

$$dU + PdV = TdS$$

$$dU = TdS - PdV$$

Thus, U can be eliminated, and we are left with four state variables, P , V , T and S . This is the reason why only four variables of state are defined. Taking two of the four state variables, P , V , T and S at a time, we get six possible pairs (P, V) , (P, T) , (P, S) , (V, T) , (V, S) and (T, S) .

The pair (P, V) is connected with an in exact differential quantity δW , as $\delta W = PdV$ and pair (T, S) with δQ as $\delta Q = TdS$. Hence after eliminating these two pairs, we are left with four pairs of thermodynamical variables (P, T) , (P, S) , (V, T) and (V, S) and Corresponding to each pair we can write a thermodynamical relation. These thermodynamical relations are known as Maxwell's thermodynamical relations.

There are four thermodynamic potentials:

(i) Internal energy, U

(ii) Helmholtz free energy, $F = U - TS$

(iii) Enthalpy $H = U + PV$

(iv) Gibbs function $G = U + PV - TS$

Each of the four Maxwell's thermodynamical relations can be derived from one of these thermodynamics potentials U , F , H and G . Only four thermodynamic potentials are defined.

1. Internal energy U. The internal energy or the intrinsic energy is the total r of the system

For an isochoric adiabatic process :

$$dU = 0$$

$$U = \text{a constant}$$

the internal energy of system remains constant in an isochoric adiabatic process.

2. Helmholtz Free Energy F. Helmholtz free energy is defined as

$$F = U - TS$$

For isothermal isochoric process :

$$dT = 0$$

$$dV = 0$$

$$dF = 0$$

$$F = \text{a constant}$$

i.e. the Helmholtz free energy remains constant during isothermal isochoric process.

3. Enthalpy H . This is known as the total heat and is given by

$$H = U + PV$$

For an isobaric adiabatic process :

$$dH = 0$$

$$H = \text{a constant}$$

i.e., enthalpy remains constant in a reversible isobaric adiabatic process.

4. Gibbs Function G or Gibbs Free Energy.

This is defined by the equation

$$G = U - TS + PV$$

(b) For an isobaric and isothermal process :

Hence, if the process is isothermal and isobaric then

$$dG = 0$$

$$G = \text{a constant}$$

Thus, Gibbs function (G) or Gibbs free energy remains constant in an isothermal-isobaric process.

Significance of Thermodynamic Potential

Since the four function U , F , H and G play in thermodynamics the same role as played by potential energy in mechanics, they are called thermodynamic potentials.

Maxwell's thermodynamical relations can be derived from the thermodynamic potentials.

Maxwell's thermodynamical relations are

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \dots\dots\dots (1)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \dots\dots\dots (2)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_P \dots\dots\dots (3)$$

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