Maxwell thermodynamic relation

This relation exist between different thermodynamic functions U, H , A and G are expressed as functions of suitably two independent variables P, V, T and S .

First thermodynamic relation

(dT/dV )S = - (dP/dS )V

Proof : In terms of internal energy , the law of thermodynamics applied as

TdS = dU + PdV

dU = TdS - PdV (1)

Where U is an internal energy , S and V are independent variables

Since dU is an exact differential , it follows from (1)

T = ( dU/dS )V

P = ( dU/dV )S

and

(dT/dV )S = - (dP/dS )V

This is called Maxwell First Thermodynamic relation .

**Second Thermodynamic relation**

(dT/dP)S = (dV/ dS )P

Proof :

In terms of enthalpy H or Total Heat

The enthalpy is defined as

dH = dU + d(PV)

= dU + PdV + VdP

= TdS + VdP (2)

Since

TdS = dU + PdV

Here H is a function of independent variables S and P. since dH is an exact differential , from (2)

We obtain

T = (dH/dS )P

V = (dH/dP)S (3)

and

(dT/dP)S = (dV/ dS )P

This is called Maxwell Second Thermodynamic relation .

**Third Thermodynamic relation**

(dP/dT)V = (dS/dV )T

**Proof** : In terms of Helmholtz free energy (A) , the equation is defined as A = U- TS

Differentiating this we get

dA = dU – TdS – SdT

= - PdV – SdT , (4)

Eq(1) gives

dU – TdS = - PdV .

In (4) A is a function of independent variables V and T . Since dA is an exact differential , it follows from (4)

P = - (dA/dV)T

S = - (dA/dT )V

and

(dP/dT )V = (dS/dV)T

This is called third Maxwell thermodynamic relation .

Fourth thermodynamic relation

(dV/ dT )P = - (dS/dP)T

Proof : In terms of Gibb’s function G is defined as

G = U – TS + PV = A + PV

On differentiating we get

dG = dA + PdV + VdP ,

Using (4) it can be written as

dG = VdP – SdT , (5)

where G is a function of independent variables P and T .In this case dG is an exact differential , so that we find

V = (dG /dP)T

S = - (dG / dT)P (6)

and

(dV/ dT )P = - (dS/dP)T

**This is called Maxwell fourth thermodynamic relation .**