Maxwell Equation :

Maxwell relations are thermodynamic equations which establish the relations between various thermodynamic quantities (e.g., pressure, P, volume, V, Entropy, S, and temperature, T) in equilibrium thermodynamics via other fundamental quantities known as thermodynamical potentials—the most important being internal energy, U, Helmholtz free energy, F, enthalpy, H, and Gibbs free energy, G.

Originally four thermodynamic relations connecting P,V,T and D were deduce by Maxwell. Two more relations have since been added. All the six are often then referred to as the thermodynamic relations. They do not constitute new low but are more deduction from the 1st law and 2nd law of thermodynamics in the equilibrium conditions. According to 1st law of thermodynamics

1- $H = U + PV$ **(Enthalpy)**

2- $G = H - TS$ **(Gibbs free energy)**

$= A + PV$

3- $A = U - TS$ **(Helmholtz free energy)**

3- $U = TS - PV$ ***(Internal Energy)***

1- Enthalpy:

H = U + PV

dH = dU + d (PV) = dU + PdV + VdP

From the first law of thermodynamic dQ = dU + dW

From the second law of thermodynamic dQ = Tds

TdS = dU + dW

$$\boxed{\mathbf{dH = TdS + VdP}}$$

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

$$\boxed{\left(\frac{\partial \boldsymbol{T}}{\partial \boldsymbol{P}}\right)\boldsymbol{s} = \left(\frac{\partial \boldsymbol{V}}{\partial \boldsymbol{S}}\right)\boldsymbol{p}}$$

2- **Helmholtz (free energy)**:

A = U –TS----------------(1)

dA = dU - d(TS) = dU - TdS – SdT ------------- (2)

From the first law of thermodynamic dQ = dU + dW

From the second law of thermodynamic dQ = Tds

TdS = dU + dW-------------(3)

Equ. (3) put in equ. (2)

$$\boxed{\mathbf{dA = -pdv - sdT}}$$

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

$$\boxed{\left(\frac{-\partial \boldsymbol{P}}{\partial \boldsymbol{T}}\right)\boldsymbol{v} = \left(\frac{-\partial \boldsymbol{S}}{\partial \boldsymbol{V}}\right)\boldsymbol{T}}$$

3- Gibbs(free energy):

G= H –TS

H= U + Pv

dG = dU + PdV + VdP - Tds – Sdt

From the first law of thermodynamic dQ = dU + dW

From the second law of thermodynamic dQ = Tds

TdS = dU + PdV
dG = TdS + VdP – TdS – SdT

$$\boxed{\textbf{dG = VdP - SdT}}$$

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

$$\boxed{\left(\frac{\partial \boldsymbol{V}}{\partial \boldsymbol{T}}\right)\boldsymbol{p} = \left(\frac{-\partial \boldsymbol{S}}{\partial \boldsymbol{P}}\right)\boldsymbol{T}}$$

4- Internai Energy:

U = TS – PV

dU = TdS – PdV

From the first law of thermodynamic dQ = dU + dW

From the second law of thermodynamic dQ = Tds

TdS = dU + PdV

$$\mathbf{dU = TdS - PdV}$$

$$(\frac{\partial N}{\partial y})\, x = (\frac{\partial M}{\partial X})\, y$$

$$\boldsymbol{(\frac{\partial T}{\partial V})\, s = - (\frac{\partial P}{\partial S})\, v}$$

This Table Summarizes the Differential Forms of the Four Types of Thermodynamic Potentials:

Thermodynamic Potentials	The Derived Derivational Form	The Maxwell equation
Internal Energy depicted by U	**dU = TdS − PdV**	$(\frac{\partial T}{\partial V})\, s = - (\frac{\partial P}{\partial S})\, v$
Enthalpy depicted by H	**dH = TdS + VdP**	$(\frac{-\partial P}{\partial T})\, v = (\frac{-\partial S}{\partial V})\, T$
Helmholtz Free Energy as depicted by F	**dF = −PdV − SdT**	$(\frac{-\partial P}{\partial T})\, v = (\frac{-\partial S}{\partial V})\, T$
Gibbs Free Energy as depicted by G	**dG = VdP − SdT**	$(\frac{\partial V}{\partial T})\, p = (\frac{-\partial S}{\partial P})\, T$

Example:

If the value of Enthalpy is 68.95 KJ and the value of Entropy is 114.2 J/K, calculate the value of free energy at the temperature 25 ^oC.

Prove for an ideal gas using Maxwell equation $(\frac{dU}{dV})\, T = zero$

du = TdS – pdV

$(\frac{\partial U}{\partial V})\, T$ = T $(\frac{\partial S}{\partial V})\, T$ – P

= T $(\frac{\partial P}{\partial T})\, v$ – P

PV = nRT for ideal gas n =1

$P = \frac{RT}{V}$

$(\frac{\partial P}{\partial T})\, v = \frac{R}{V}$

$(\frac{\partial \mathrm{U}}{\partial \mathrm{V}})\, \mathrm{T} = T\, \frac{R}{V} - P$

= p – p = zero

2- Prove that $\left(\frac{\partial \boldsymbol{H}}{\partial \boldsymbol{V}}\right)\boldsymbol{T} = \boldsymbol{Zero}$

H= U+ Pv

dH = dU + PdV + vdP

dH = dQ + VdP

= TdS + VdP

$(\frac{\partial H}{\partial V})\, T = T\, (\frac{\partial S}{\partial V})\, T + V\, (\frac{\partial P}{\partial V})\, T$

$= (\frac{\partial P}{\partial T})\, v + V\, (\frac{-RT}{V^2})$

= T $(\frac{R}{V}) - (\frac{-RT}{V})$

$(\frac{\partial H}{\partial V})\, T = zero$

3-Prove that $(\frac{\partial A}{\partial V})T = -P$

dA = -PdV – SdT

$$(\frac{\partial A}{\partial V})T = -P - S\ (\frac{\partial T}{\partial V})T$$

T = Constant-----------------dT = Zero

$$(\frac{\partial A}{\partial V})T = -P$$

4-Prove that $\left(\frac{\partial \boldsymbol{H}}{\partial \boldsymbol{p}}\right)\boldsymbol{T} = \boldsymbol{Zero}$

H= U+ Pv

dH = dU + PdV + vdP

dH = dQ + VdP

= TdS + VdP

$$\left(\frac{\partial H}{\partial P}\right)T = \mathrm{T}\left(\frac{\partial S}{\partial P}\right)T + V$$

$$= -\mathrm{T}\left(\frac{\partial V}{\partial T}\right)P + V$$

PV = n RT for an ideal gas n=1

$$(\frac{\partial \mathrm{V}}{\partial \mathrm{T}})\ \mathrm{P} = \frac{\mathrm{R}}{\mathrm{P}}$$

$$(\frac{\partial H}{\partial P})T = -T\ (\frac{R}{P}) + v$$

$$(\frac{\partial H}{\partial P})T = Zero$$