

**Udai Pratap (Autonomous) College, Varanasi****E-learning Material**

<b>Module/ Lecture</b>	<b>06</b>
<b>Topic</b>	<b>Maxwell's Thermodynamic Relations</b>
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## Maxwell's Thermodynamic Relations

From first law of thermodynamics

$$\begin{aligned}\delta Q &= dU + \delta W \\ dU &= \delta Q - pdV\end{aligned}\tag{1}$$

From second law of thermodynamics

$$\delta Q = TdS\tag{2}$$

Combining Eqs. (1) and (2), we get

$$dU = TdS - pdV\tag{3}$$

Eqn. (3) is known as Gibb's Equation. It involves only point functions  $p$ ,  $V$ ,  $T$ ,  $S$  and  $U$  and also these are perfect (exact) differential.

Considering  $U$ ,  $S$  and  $V$  to be the function of any two independent variables  $x$  and  $y$

$$U=U(x, y), \quad S=S(x, y), \quad V=V(x, y)$$

Thus

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy\tag{4a}$$

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy\tag{4b}$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy\tag{4c}$$

On substituting these values of  $dU$ ,  $dS$  and  $dV$  in Eqn. (3), we get

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left(\frac{\partial S}{\partial x}\right)_y dx + T\left(\frac{\partial S}{\partial y}\right)_x dy - p\left(\frac{\partial V}{\partial x}\right)_y dx - p\left(\frac{\partial V}{\partial y}\right)_x dy$$

Comparing Coefficients of  $dx$  and  $dy$  on both sides

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - p\left(\frac{\partial V}{\partial x}\right)_y\tag{5a}$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - p\left(\frac{\partial V}{\partial y}\right)_x \quad (5b)$$

Since U, V and S are perfect differentials of x and y, we must have

$$\frac{\partial^2 U}{\partial y \partial x} = \frac{\partial^2 U}{\partial x \partial y}, \quad \frac{\partial^2 V}{\partial y \partial x} = \frac{\partial^2 V}{\partial x \partial y}, \quad \frac{\partial^2 S}{\partial y \partial x} = \frac{\partial^2 S}{\partial x \partial y} \quad (6)$$

The differentiating partially to Eq. (5a) w.r.t. y and Eq (5b) with respect to x and then using Eq. (6), we get

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial p}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial p}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \quad (7)$$

Equation (7) is the general expression for Maxwell's thermodynamic relations in terms of x and y. The four Maxwell's relations can be deduced with the help of this equation by taking x and y as any of the two variables from set p, V, T and S. It is preferable to take one thermal (S or T) and one mechanical variable (V or p). Thus the possible pairs (i) x=S and y=V; (ii) x=S and y=p; (iii) x=T and y=V; (iv) x=T, y=p leads to the four Maxwell's relations.

**Case-1:** Taking x=S, y=V, we have  $\left(\frac{\partial V}{\partial S}\right)_V = \left(\frac{\partial S}{\partial V}\right)_S = 0$  and  $\left(\frac{\partial V}{\partial V}\right)_S = \left(\frac{\partial S}{\partial S}\right)_V = 1$

and Eq. (7) gives

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (8)$$

Eq. (8) gives first Maxwell's Thermodynamic relation.

**Case-2:** Taking x=S, y=p, we have  $\left(\frac{\partial p}{\partial S}\right)_p = \left(\frac{\partial S}{\partial p}\right)_S = 0$  and  $\left(\frac{\partial p}{\partial p}\right)_S = \left(\frac{\partial S}{\partial S}\right)_p = 1$

and Eq. (7) gives

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (9)$$

Eq. (9) gives second Maxwell's Thermodynamic relation.

**Case-3:** Taking  $x=T, y=V$ , we have  $\left(\frac{\partial V}{\partial T}\right)_V = \left(\frac{\partial T}{\partial V}\right)_T = 0$  and  $\left(\frac{\partial V}{\partial V}\right)_T = \left(\frac{\partial T}{\partial T}\right)_V = 1$

and Eq. (7) gives

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (10)$$

Eq. (10) gives Third Maxwell's Thermodynamic relation.

**Case-4:** Taking  $x=T, y=p$ , we have  $\left(\frac{\partial p}{\partial T}\right)_p = \left(\frac{\partial T}{\partial p}\right)_T = 0$  and  $\left(\frac{\partial p}{\partial p}\right)_T = \left(\frac{\partial T}{\partial T}\right)_p = 1$

and Eq. (7) gives

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (11)$$

Eq. (11) gives fourth Maxwell's Thermodynamic relation.

Equations (8) –(11) are four Maxwell's Thermodynamic relations.

**Note:** Also there are two more relations  $x$  &  $y$  taken as  $p$  &  $V$  (Mechanical variables) or  $T$  &  $S$  (Thermal variables).

1. If  $x=p, y=V$ , we have  $\left(\frac{\partial p}{\partial V}\right)_p = \left(\frac{\partial V}{\partial p}\right)_V = 0$  and  $\left(\frac{\partial p}{\partial p}\right)_V = \left(\frac{\partial V}{\partial V}\right)_p = 1$

and Eq. (7) gives

$$\left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial S}{\partial V}\right)_p - \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial S}{\partial p}\right)_V = 1 \quad (12)$$

2. If  $x=T, y=S$ , we have  $\left(\frac{\partial T}{\partial S}\right)_T = \left(\frac{\partial S}{\partial T}\right)_S = 0$  and  $\left(\frac{\partial T}{\partial T}\right)_S = \left(\frac{\partial S}{\partial S}\right)_T = 1$

and Eq. (7) gives

$$\left(\frac{\partial p}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial p}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1 \quad (13)$$

Eqs. (13 & 14) are known as Maxwell's Identities.

## Thermodynamic Functions or Potentials

The properties of a four substances can conveniently be represented in terms of four functions, Internal energy (U), Enthalpy (H), Helmholtz function (F) and Gibb's function (G).

Internal energy (U), Enthalpy (H), Helmholtz function (F) and Gibb's function (G) are called thermodynamic potentials of the system because the thermodynamic variables  $p$ ,  $V$ ,  $T$  and  $S$  can be obtained by differentiating them w. r. t. the independent quantities related to them. It is analogous to the intensity of a field which can be obtained by the space differentiation of related potential.

**(i) Internal energy (U) :** According to first and second law of thermodynamics, the change in internal energy

$$\begin{aligned}dU &= \delta Q - \delta W \\dU &= TdS - pdV\end{aligned}\tag{1}$$

Physically,  $dU$  is increment in energy of a system, if that much adiabatic work is done on it. Internal energy is the quantity of energy in a system which remains constant during an adiabatic - isochoric process.

**(ii) Enthalpy (H):** It is a property of thermodynamic system given by the mathematical expression

$$H = U + pV$$

This is known as total heat function (energy function).

Change in Enthalpy,

$$\begin{aligned}dH &= dU + pdV + Vdp \\&= TdS - pdV + pdV + Vdp && \text{(since } dU = TdS - pdV \text{)} \\dH &= TdS + Vdp\end{aligned}\tag{2}$$

Physically Enthalpy is the quantity of energy in a system which remains constant during the throttling process (adiabatic-isobaric process).

**(iii) Helmholtz-function (F):** Helmholtz function is defined as

$$F=U-TS$$

Change in Helmholtz function

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= TdS - pdV - TdS - SdT \quad (\text{since } dU = TdS - pdV) \end{aligned}$$

i.e.  $dH = -pdV - SdT$  (3)

Physically Helmholtz function is the quantity of energy in a system which remains constant during the isothermal-isochoric process.

Also for reversible isothermal process from Eq. (3) we get

$$dH = -pdV$$

i.e. change in Helmholtz function during a reversible isothermal process is equal to the work done on the system.

**(iv) Gibb's-function (G):** Helmholtz function is defined as

$$\begin{aligned} G &= H - TS \\ &= U + pV - TS \end{aligned}$$

Change in Gibb's function

$$\begin{aligned} dG &= dU + pdV + Vdp - TdS - SdT \\ &= TdS + pdV + Vdp - pdV - TdS - SdT \quad (\text{since } dU = TdS - pdV) \end{aligned}$$

i.e.  $dG = Vdp - SdT$  (4)

Physically Gibb's function is the quantity of energy in a system which remains constant during the isothermal-isobaric process. From Equations (1-4) we also see that  $U=U(S, V)$ ;  $H=H(S, p)$ ;  $F=F(T, V)$  and  $G=G(T, p)$ .

## Derivation of Maxwell's Relations using Thermodynamic Potentials

Since thermodynamic potentials U, H, F and G are point functions and their differentiations are exact differential.

(i) Since

$$dU = TdS - pdV \quad (1)$$

thus

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad (2)$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \quad (3)$$

As U is perfect differential, we have

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

Thus Eqs. (2 & 3) gives

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (4)$$

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

This is first Maxwell's Thermodynamic relation.

(ii) Since

$$dH = TdS + VdP \quad (5)$$

thus

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad (6)$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V \quad (7)$$

As H is perfect differential, we have

$$\frac{\partial^2 H}{\partial p \partial S} = \frac{\partial^2 H}{\partial S \partial p}$$

Thus Eqs. (6 & 7) gives

$$\left( \frac{\partial T}{\partial p} \right)_S = \left( \frac{\partial V}{\partial S} \right)_p \quad (8)$$

This is second Maxwell's Thermodynamic relation.

**(iii).** Since

$$dF = -SdT - pdV \quad (9)$$

thus

$$\left( \frac{\partial F}{\partial T} \right)_V = -S \quad (10)$$

$$\left( \frac{\partial F}{\partial V} \right)_T = -p \quad (11)$$

As F is perfect differential, we have

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}$$

Thus Eqs. (10 & 11) gives

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V \quad (12)$$

This is third Maxwell's Thermodynamic relation.

**(iv).** Since

$$dG = Vdp - SdT \quad (13)$$

thus

$$\left( \frac{\partial G}{\partial T} \right)_p = -S \quad (14)$$

$$\left( \frac{\partial G}{\partial p} \right)_T = V \quad (15)$$



As  $G$  is perfect differential, we have

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}$$

Thus Eqs. (14 & 15) gives

$$\left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p \quad (16)$$

This is fourth Maxwell's Thermodynamic relation.