

Monad University, Hapur

Programme Name- B.Tech (ME)

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Subject Name- Applied Thermodynamics

Topic:- Thermodynamics Relation

Sub Topic:- Maxwell Equation

Thermodynamics Relation

Some Mathematics theorems:-

Theorem 1:- If a relation exists among the variables x,y and z, then z may be expressed as a function of x and y.

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

if $\left(\frac{\partial z}{\partial x}\right)_y = M$ and $\left(\frac{\partial z}{\partial y}\right)_x = N$, then $dz = Mdx + Ndy$ is called exact differential equation. Where M & N are the function of x and y.

And $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$ this is the condition of exact differential equation.

Theorem 2:- If a quantity f is a function of x,y and z and a relation exist among x,y and z , then f is a function of any two of the x, y and z. Similarly any one of x,y and z may be regarded to be a function of f and any one of x,y and z.

Thus, if $x = x(f,y)$

$$dx = \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f dy$$

$$\text{and } \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1$$

Theorem 3:- Among the variables x,y and z any one variable may be considered as a function of other two, thus

$$x = x(y,z)$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$\text{and } \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

Maxwell Equation

We know that from 1st Law of thermodynamics

$$du = Q - PdV \dots\dots\dots(a)$$

from theorem 1

$$\text{If } dz = Mdx + Ndy \dots\dots\dots(b), \text{ then } \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

After comparing equation (a) and (b)

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \dots\dots\dots(1)$$

We know that from enthalpy equation

$$dH = U + PV$$

After differentiating above equation

$$dH = du + PdV + v dP$$

$$dH = dQ + v dP$$

$$dH = T ds + v dP \dots\dots\dots(c)$$

After comparing equation (b) and (c)

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \dots\dots\dots(2)$$

From Helmholtz function.

$$F = U - TS$$

After differentiating above equation

$$dF = dU - Tds - sdT$$

$$dF = -pdv - sdT \dots\dots\dots(d)$$

After comparing equation (b) and (d)

$$-\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial s}{\partial v}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \dots\dots\dots(3)$$

From Gibbs function :-

$$G = H - TS$$

After differentiating above equation

$$dG = dH - Tds - sdT$$

$$dG = vdp - sdT \dots\dots\dots(e)$$

After comparing equation (e) and equation (b)

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \dots\dots\dots(4)$$

The above four equations (1),(2),(3) and (4) are called Maxwell Equation.

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \dots\dots\dots(1)$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \dots\dots\dots(2)$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \dots\dots\dots(3)$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \dots\dots\dots(4)$$