

Maxwell relation, $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

We know, $dH = Tds + VdP$

If P is constant, $dP = 0$

$$dH = Tds$$

$$\text{or } \left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{--- (1)}$$

If S is constant, $dS = 0$

From eqⁿ $dH = Tds + VdP$

$$\left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{--- (2)}$$

On differentiating eqⁿ (1) w.r. to P where S is constant

$$\frac{\partial^2 H}{(\partial S)_P (\partial P)_S} = \left(\frac{\partial T}{\partial P}\right)_S \quad \text{--- (3)}$$

And eqⁿ (2) is differentiating w.r. to S where P is constant

$$\frac{\partial^2 H}{(\partial P)_S (\partial S)_P} = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{--- (4)}$$

From equation (3) and equation (4), we have.

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{--- (5)}$$

The above equation (5) is also Maxwell relation.

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Maxwell relation: - $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

We know $dA = -SdT - PdV$

When T is constant, $dT = 0$

$$\therefore \left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{--- (1)}$$

When V is constant, $dV = 0$

$$\text{eqn } dA = -SdT - PdV$$

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

Differentiating equation (1) w.r. to T , where V is constant.

$$\frac{\partial^2 A}{(\partial V)_T (\partial T)_V} = -\left(\frac{\partial P}{\partial T}\right)_V \quad \text{--- (3)}$$

Again differentiating equation (2) with respect to V , where T is constant.

$$\frac{\partial^2 A}{(\partial T)_V (\partial V)_T} = -\left(\frac{\partial S}{\partial V}\right)_T \quad \text{--- (4)}$$

From equation (3) and (4) we have.

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

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

The above relation is also Maxwell relation.

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Maxwell relation, :- $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

4th

We know $dG = -SdT + VdP$

When T is const, $dT = 0$

$$\therefore dG = VdP$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{--- (1)}$$

$\therefore dG = -SdT + VdP$

When pressure P is constant $dP = 0$

$$\therefore dG = -SdT$$

$$\text{or } \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{--- (2)}$$

Differentiating eq. (1) w.r. to T where P is const.

$$\frac{\partial^2 G}{(\partial P)_T (\partial T)_P} = \left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (3)}$$

Differentiating eq. (2) w.r. to P , where T is constant

$$\frac{\partial^2 G}{(\partial T)_P (\partial P)_T} = -\left(\frac{\partial S}{\partial P}\right)_T \quad \text{--- (4)}$$

From equation (3) and equation (4)

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

$$\text{or } \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (5)}$$

The above eq. is also Maxwell relation.



5th

Maxwell relation, $\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$

To derive Maxwell relation the following two eqⁿ are important.

$$dU = Tds - PdV \quad \text{--- (i)}$$

$$dH = Tds + VdP \quad \text{--- (ii)}$$

Consider eqⁿ $dU = Tds - PdV$

If V is constant, then $dV = 0$

$$dU = Tds$$

$$\text{or } \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{--- (1)}$$

Consider eqⁿ $dH = Tds + VdP$

When Pressure P is constant, $dP = 0$

$$dH = Tds$$

$$\text{or } \left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{--- (2)}$$

From equation (1) and equation (2)

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$$

The above eqⁿ is also Maxwell relation.

6th

Maxwell relation: - $\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T$

We know $dU = Tds - PdV$ — (a)

$dA = -SdT - PdV$ — (b)

Consider eqⁿ $dU = Tds - PdV$

If S is constant $ds = 0$

$\left(\frac{\partial U}{\partial V}\right)_S = -P$ — (1)

From eqⁿ $dA = -SdT - PdV$

If T is constant, $dT = 0$

$\therefore \left(\frac{\partial A}{\partial V}\right)_T = -P$ — (2)

From eqⁿ (1) and (2) $\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T$ Proved

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Prove, $\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$

7th

We know, $dH = Tds + VdP$

$dG = -SdT + VdP$

When S is constant, $ds = 0$

$\therefore dH = Tds + VdP$

$\therefore \left(\frac{\partial H}{\partial P}\right)_S = V$ — (1)

$dG = -SdT + VdP$

When T is constant, $dT = 0$

$\left(\frac{\partial G}{\partial P}\right)_T = V$ — (2)

From equation (1) and (2), we have

$\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$

It is also Maxwell relation.

8th x

Prove. $\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P$

Consider eqⁿ $da = -s dt - PdV$ — (a)
 $du = -s dt + VdP$ — (b)

Consider eqⁿ $da = -s dt - PdV$
when V is constant $dV = 0$

$$\left(\frac{\partial A}{\partial T}\right)_V = -s \quad \text{--- (1)}$$

Consider eqⁿ $du = -s dt + VdP$

when P is constant, $dP = 0$

$$\left(\frac{\partial G}{\partial T}\right)_P = -s \quad \text{--- (2)}$$

from eqⁿ (1) and (2)

$$\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P$$

Proved.