Maxwell's Thermodynamic Relation

Maxwell derived the relation by combining 1st & 2nd law of thermodynamics for a PVT system undergoing an infinitesimal reversible process.

We have from 1st law of thermodynamics,

$$dQ = dU + dW$$

$$\Rightarrow dQ = dU + pdV$$

$$\therefore \ dU = dQ - pdV \qquad \text{---------- (i)}$$

From second law of thermodynamics,

$$dS = \frac{dQ}{T}$$

$$\Rightarrow dQ = TdS$$

$$\therefore \ dU = TdS - pdV \qquad \text{---------- (ii)}$$

Considering U, S & V are $function$ of two independent variables x & y.

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

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

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

Substituting their value in eq. (ii) we have-

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

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

Comparing the coefficient of dx & dy from equation (iii) we have-

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \qquad \text{---------- (iv)}$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_y - P\left(\frac{\partial V}{\partial y}\right)_x \qquad \text{---------- (v)}$$

Differentiating equation (iv) & (v) with respect to y & x we have-

$$\frac{\partial^2 U}{\partial y\cdot\partial x} = \left(\frac{\partial T}{\partial y}\right)_x \cdot \left(\frac{\partial S}{\partial x}\right)_y + T\cdot\frac{\partial^2 S}{\partial y\cdot\partial x} - \left(\frac{\partial p}{\partial y}\right)_x \cdot \left(\frac{\partial U}{\partial x}\right)_x - p\left(\frac{\partial^2 V}{\partial y\cdot\partial x}\right)$$

$$\frac{\partial^2 U}{\partial x\cdot\partial y} = \left(\frac{\partial T}{\partial x}\right)_y \cdot \left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x\cdot\partial y} - \left(\frac{\partial p}{\partial x}\right)_y \cdot \left(\frac{\partial U}{\partial y}\right)_x - p\left(\frac{\partial^2 V}{\partial y\cdot\partial x}\right)$$

Since dU is a perfect differential, above two expressions are equal $\dfrac{\partial^2 U}{\partial y\cdot\partial x} = \dfrac{\partial^2 U}{\partial x\cdot\partial y}$ and single dS & dV are perfect differential.

After simplifying we can write,

$$\left(\frac{\partial T}{\partial y}\right)_x \cdot \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial p}{\partial y}\right)_x \cdot \left(\frac{\partial U}{\partial x}\right)_x = \left(\frac{\partial T}{\partial x}\right)_y \cdot \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial p}{\partial x}\right)_y \cdot \left(\frac{\partial U}{\partial y}\right)_x \qquad \text{------ (vi)}$$

Equation (vi) is the general equation for Maxwell's thermodynamic Relation.

1st Relation:

Putting $x = T$, $y = V$ and taking T & V as independent variables.

$$\frac{\partial T}{\partial x} = 1,\ \frac{\partial V}{\partial y} = 1,\ \frac{\partial T}{\partial y} = 0,\ \frac{\partial V}{\partial x} = 0$$

(vi) $\Rightarrow \left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$ $\qquad \left[But, dS = \dfrac{dQ}{T}\right]$

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

For a thermodynamic system, the increase of entropy per unit increase of volume at constant temperature is equal to the increase of temperature in a isochoric process.

2nd Relation:

Taking T & P are independent variables.   i.e.   x=T & y=P

We get from (vi)

$$\frac{\partial T}{\partial x} = 1,\ \frac{\partial P}{\partial y} = 1\ \&\ \frac{\partial T}{\partial y} = 0,\ \frac{\partial P}{\partial x} = 0$$

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

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

The decrease of entropy per unit increase of pressure in a isothermal process is equal to the increase of volume per unit increase of temperature for a isobaric process.

3rd Relation:

Taking entropy & volume as independent variables.   i.e.   x=S & y=V

We get,

$$\frac{\partial S}{\partial x} = 1, \ \frac{\partial V}{\partial y} = 1 \ \& \ \frac{\partial S}{\partial y} = 0, \ \frac{\partial V}{\partial x} = 0$$

From equation (vi) we can write,

$$\left(\frac{\partial T}{\partial x}\right)_S = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$\Rightarrow \left(\frac{\partial T}{\partial x}\right)_S = -T\left(\frac{\partial P}{\partial Q}\right)_v$$

The increase of temperature per unit increase of volume in a reversible adiabatic process is equal to the decrease of pressure per unit increase of entropy in a isochoric process.

4th Relation:

Taking entropy & Pressure as independent variable.   i.e.   x=S & y=P

We have,

$$\frac{\partial S}{\partial x} = 1, \ \frac{\partial P}{\partial y} = 1 \ \& \ \frac{\partial S}{\partial y} = 0, \ \frac{\partial P}{\partial x} = 0$$

(vi) $$\Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial v}{\partial S}\right)_p$$

$$\Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = T\left(\frac{\partial v}{\partial Q}\right)_p$$

The increase of temperature per unit increase pressure in a reversible adiabatic process is equal to the increase of volume per unit increase of entropy in a isobaric process.

5th Relation:

Taking p & v as independent variable.   i.e.   x=p & y=v

We get,

$$\frac{\partial p}{\partial x} = 1, \ \frac{\partial v}{\partial y} = 1 \ \& \ \frac{\partial p}{\partial y} = 0, \ \frac{\partial v}{\partial x} = 0$$

(vi) $\Rightarrow \left(\frac{\partial T}{\partial p}\right)_v \cdot \left(\frac{\partial S}{\partial v}\right)_v - \left(\frac{\partial T}{\partial v}\right)_p \cdot \left(\frac{\partial S}{\partial p}\right)_v = 1$

6th Relation:

Taking T & S as independent variable.   i.e.   x=T & y=S

We get,

$$\frac{\partial T}{\partial x} = 1, \ \frac{\partial S}{\partial y} = 1 \ \& \ \frac{\partial T}{\partial y} = 0, \ \frac{\partial S}{\partial x} = 0$$

(vi) $\Rightarrow \left(\frac{\partial p}{\partial T}\right)_S \cdot \left(\frac{\partial v}{\partial S}\right)_T - \left(\frac{\partial p}{\partial S}\right)_T \cdot \left(\frac{\partial v}{\partial T}\right)_S = 1$

Clausius – Clapeyron equation (1st latent heat equation)

From Maxwell's 1st relation we can write

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial P}{\partial t}\right)_v$$

$$\Rightarrow T \left(\frac{\partial S}{\partial v}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_v \qquad [\because dQ = TdS]$$

$$\Rightarrow \left(\frac{\partial Q}{\partial v}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_v \qquad \text{----------- (i)}$$

Here, $\left(\frac{\partial Q}{\partial v}\right)_T$ represents the quantity of heat absorbed per unit increase in volume at constant temperature. This quantity of heat absorbed at constant temperature is the latent heat (L),

Thus $dQ = L \ \& \ dV = V_2 - V_1$

$$\therefore \left(\frac{L}{V_2 - V_1}\right)_T = T \left(\frac{dp}{dT}\right)_V$$

$$\Rightarrow \left(\frac{dp}{dT}\right) = \frac{L}{T(V_2 - V_1)} \ \text{ which is the 1}^{st} \text{ latent heat equation.}$$

==Specific heat of constant volume Cv:==

The amount of heat required to raise the temperature of unit mass of a gas through 1°C when its volume keep constant, it is represented by $C_v = \left(\frac{\Delta Q}{\Delta T}\right)_v$

==Specific heat of constant== **Pressure** C_p: The amount of heat required to raise the temperature of unit mass of a gas through 1°C when its pressure keep constant, it is represented by $C_p = \left(\frac{\Delta Q}{\Delta T}\right)_p$

Show that $\quad C_p - C_v = R$

If V & T are chosen as the independent variables $U = f(V, T)$ ------------ (i)

Differentiating (i)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \text{------------(ii)}$$

According to the 1st law of thermodynamics-

$$dQ = dU + dW$$

$$= dU + pdV$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV \text{ ---------------(iii)}$$

Dividing both side by dT

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\}\frac{dV}{dT} \text{ ------------------ (iv)}$$

If the gas is heated at constant volume-

$$\left(\frac{\partial Q}{\partial T}\right)_V = C_V \ \& \ \frac{dV}{dT} = 0$$

$$\left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \text{ -------------------- (v)}$$

When the gas is heated at constant pressure,

$$\frac{dQ}{dT} = C_p$$

$$\therefore C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\}\left(\frac{\partial V}{\partial T}\right)_p$$

Composed by: KN, ARB

$$\therefore C_p = C_V + \left\{ p + \left(\frac{\partial U}{\partial V} \right)_T \right\} \left(\frac{\partial V}{\partial T} \right)_p$$

But $\left(\frac{\partial U}{\partial V} \right)_T = 0$

For ideal gas equation we can write

$$PV = RT$$

$$\Rightarrow P \left(\frac{\partial V}{\partial T} \right)_p = R$$

$$\therefore C_p - C_V = P \cdot \left(\frac{\partial V}{\partial T} \right)_p + \left(\frac{\partial U}{\partial V} \right)_T \cdot \left(\frac{\partial V}{\partial T} \right)_*$$

$$\Rightarrow C_p - C_V = R \qquad \text{(\underline{Shown})}$$

Maxwell's law of Equipartition energy:

According to kinetic theory of gas we can write,

$$\frac{1}{2} mc^2 = \frac{3}{2} kT$$

But, $c^2 = u^2 + v^2 + w^2$ as x, y, z are all equivalent. Mean square velocities along three axes are equal.

$$u^2 = v^2 = w^2$$

Hence,

$$u^2 = v^2 = w^2 = \frac{1}{3} c^2$$

$$\therefore \frac{1}{2} mu^2 = \frac{1}{2} mv^2 = \frac{1}{2} mw^2$$

$$\therefore \frac{1}{2} mc^2 = 3 \left(\frac{1}{2} mu^2 \right) = \left(\frac{1}{2} mv^2 \right) = \left(\frac{1}{2} mw^2 \right) = \frac{3}{2} kT$$

$$\Rightarrow 3 \left(\frac{1}{2} mu^2 \right) = \frac{3}{2} kT \qquad \text{or,} \ \frac{1}{2} mu^2 = \frac{1}{2} kT$$

$$\Rightarrow 3 \left(\frac{1}{2} mv^2 \right) = \frac{3}{2} kT \qquad \text{or,} \ \frac{1}{2} mv^2 = \frac{1}{2} kT$$

$$\Rightarrow 3\left(\frac{1}{2}mw^2\right) = \frac{3}{2}kT \qquad \text{or,} \ \frac{1}{2}mw^2 = \frac{1}{2}kT$$

Thus, the average K.E. associated with each degree of freedom $= \frac{1}{2}kT$