Entropy of Perfect Gas :-

When we have value of V and T

Consider 1 mole gas $PV = RT$

Let dQ energy is given to the gas

$$dQ = dU + dW$$

$$dQ = Tds$$

$$dU = C_v dT$$

$$dW = PdV$$

$$Tds = C_v dT + PdV.$$

$$PV = RT \Rightarrow P = RT/V$$

$$Tds = C_v dT + RT \frac{dV}{V}$$

$$ds = C_v \frac{dT}{T} + \frac{R\cancel{T}}{\cancel{T}} \frac{dV}{V}$$

$$= C_v \frac{dT}{T} + R \frac{dV}{V}$$

$$\int_{S_1}^{S_2} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}.$$

$$\boxed{S_2 - S_1 = C_v \ln T_2/T_1 + R \ln V_2/V_1}$$

This equation is in terms of volume and temperature when we have value of P and T

$$T\,ds = C_v\,dT + \underline{P\,dV}.$$

$$PV = RT$$

$$P\,dV + V\,dP = R\,dT$$

$$P\,dV = R\,dT - V\,dP$$

$$T\,ds = C_v\,dT + R\,dT - V\,dP$$

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

$$ds = (C_v+R)\left(\frac{dT}{T}\right) - \frac{V}{T}\,dP.$$

$$= (C_v+R)\,\frac{dT}{T} - \frac{R\cancel{T}}{P\cancel{T}}\,dP$$

$$ds = (C_v+R)\,\frac{dT}{T} - R\,\frac{dP}{P}$$

$$\int_{S_1}^{S_2} ds = (C_v+R)\int_{T_1}^{T_2}\frac{dT}{T} - R\int_{P_1}^{P_2}\frac{dP}{P}$$

$$\boxed{S_2 - S_1 = (C_v+R)\ln T_2/T_1 - R\ln P_2/P_1}$$

When we have value of P and T of the process. (initial and final)

Tds Equations:

1st Tds Equation:

$$S = S(T, V)$$

$$dS = \left.\frac{\partial S}{\partial T}\right|_V dT + \left.\frac{\partial S}{\partial V}\right|_T dV$$

$T\,dS = dQ$

$\left.\frac{\partial Q}{\partial T}\right|_V = C_V$

Let us multiply it by T

$$T\,dS = T\left.\frac{\partial S}{\partial T}\right|_V dT + T\left.\frac{\partial S}{\partial V}\right|_T dV$$

$$= C_V\,dT + T\left.\frac{\partial S}{\partial V}\right|_T dV.$$

$$\boxed{\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V \quad \text{using 1st Maxwell equation}}$$

$$\boxed{T\,dS = C_V\,dT + T\left.\frac{\partial P}{\partial T}\right|_V dV.}$$

1st Tds Equation.

2nd Tds Equation

$$S = S(T, P)$$

$$ds = \frac{\partial s}{\partial T}\Big|_P dT + \frac{\partial s}{\partial P}\Big|_T dP$$

$$T\,ds = T\frac{\partial s}{\partial T}\Big|_P dT + T\frac{\partial s}{\partial P}\Big|_T dP$$

$$= C_p\,dT + T\frac{\partial s}{\partial P}\Big|_T dP$$

using Maxwell Eq. $\frac{\partial s}{\partial P}\Big|_T = -\frac{\partial V}{\partial T}\Big|_P$

$$\boxed{T\,ds = C_p\,dT - T\frac{\partial V}{\partial T}\Big|_P dP}$$

2nd Tds Equation.

<u>3rd Tds equation:</u>

$$s = s(P, V)$$

and following the above similar steps.

$ds = \frac{\partial s}{\partial P}\Big|_V dP + \frac{\partial s}{\partial V}\Big|_P dV$ or $T\,ds = T\frac{\partial s}{\partial P}\Big|_V dP + T\frac{\partial s}{\partial V}\Big|_P dV$

so $T\,ds = T\frac{\partial s}{\partial T}\Big|_V \frac{\partial T}{\partial P}\Big|_V dP + T\frac{\partial s}{\partial T}\Big|_P \frac{\partial T}{\partial V}\Big|_P dV$

$$\boxed{T\,ds = C_v\frac{\partial T}{\partial P}\Big|_V dP + C_p\frac{\partial T}{\partial V}\Big|_P dV}$$

3rd Tds equation.

Heat Capacity Equation :-

As we know from two Tds Equation

$$C_v\,dT + T\frac{\partial P}{\partial T}\Big|_V dV = C_p\,dT - T\frac{\partial V}{\partial T}\Big|_P dP$$

$$(C_p - C_v)\,dT = T\left[\frac{\partial P}{\partial T}\Big|_V dV + \frac{\partial V}{\partial T}\Big|_P dP\right]$$

$$dT = \frac{T}{C_p - C_v}\left[\frac{\partial P}{\partial T}\Big|_V dV + \frac{\partial V}{\partial T}\Big|_P dP\right]$$

$$T = T(P, V)$$

$$dT = \frac{\partial T}{\partial P}\Big|_V dP + \frac{\partial T}{\partial V}\Big|_P dV.$$

$$\frac{\partial T}{\partial P}\Big|_V dP + \frac{\partial T}{\partial V}\Big|_P dV = \frac{T}{C_p - C_v}\left[\frac{\partial P}{\partial T}\Big|_V dV + \frac{\partial V}{\partial T}\Big|_P dP\right]$$

from above we get :

$$\left.\frac{\partial T}{\partial P}\right|_V = \frac{T}{C_p - C_v} \left.\frac{\partial V}{\partial T}\right|_P \quad \text{—— (1)}$$

and

$$\left.\frac{\partial T}{\partial V}\right|_P = \frac{T}{C_p - C_v} \left.\frac{\partial P}{\partial T}\right|_V \quad \text{—— (2)}$$

If we multiply above two equations and rearrange

$$\boxed{C_p - C_v = T \left.\frac{\partial V}{\partial T}\right|_P \left.\frac{\partial P}{\partial T}\right|_V} \quad \text{—— (A)}$$

Two other forms of Heat capacity equations are achieved from condition that if

$$f(x, y, z) = 0$$

then $\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1$

we know $f(P, V, T) = 0$

so $\left.\frac{\partial P}{\partial V}\right|_T \cdot \left.\frac{\partial V}{\partial T}\right|_P \cdot \left.\frac{\partial T}{\partial P}\right|_V = -1$

So $\left.\frac{\partial P}{\partial T}\right|_V = - \left.\frac{\partial V}{\partial T}\right|_P \left.\frac{\partial P}{\partial V}\right|_T$

Putting this value of $\left.\frac{\partial P}{\partial T}\right|_V$ in eq A

$$\boxed{C_p - C_v = T \left.\frac{\partial V}{\partial T}\right|_P \left.\frac{\partial P}{\partial T}\right|_V} \qquad A$$

$$\boxed{C_p - C_v = -T \left(\left.\frac{\partial V}{\partial T}\right|_P\right)^2 \left.\frac{\partial P}{\partial V}\right|_T}$$

Imp Equation

Similarly we can get value of

$$\left.\frac{\partial V}{\partial T}\right|_P = - \left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial V}{\partial P}\right|_T$$

and then from eq A

$$\boxed{C_p - C_v = -T \left(\left.\frac{\partial P}{\partial T}\right|_V\right)^2 \left.\frac{\partial V}{\partial P}\right|_T}$$

Imp Equation

$$\begin{array}{ccc} 1 & \rightarrow & 2 \\ \uparrow & & \downarrow \\ 4 & \leftarrow & 3 \end{array} \qquad \begin{array}{ccc} S & \rightarrow & P \\ \uparrow & & \downarrow \\ V & \leftarrow & T \end{array}$$

Move the position of S according to these numbers

Surest Process To Verify

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V \qquad \left.\frac{\partial V}{\partial T}\right|_P = -\left.\frac{\partial S}{\partial P}\right|_T \qquad \left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial V}{\partial S}\right|_P \qquad \left.\frac{\partial P}{\partial S}\right|_V = -\left.\frac{\partial T}{\partial V}\right|_S$$

+ve 1 | −ve | +ve | −ve

when P and T together then the equation is +ve else −ve.