# Thermodynamic Relations

**Theorem 1**

$$dz = Mdx + Ndy$$

exact
$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

**Theorem 2:-**

$$F = \phi(x, y, z)$$

$$\left(\frac{\partial x}{\partial y}\right)_F \left(\frac{\partial y}{\partial z}\right)_F \left(\frac{\partial z}{\partial x}\right)_F = +1$$

**Theorem 3:**

$$PV = mRT$$

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

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -1$$

## Maxwell's equation:-

1

$$Tds = du + Pdv$$

$$du = Tds - Pdv$$

$$dz = Mdx + Ndy$$

$M \rightarrow T$

$x \rightarrow S$

$N \rightarrow -P$

$y \rightarrow V$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$\boxed{\left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial P}{\partial s}\right)_V} \quad (1)$$

(2)

$$Tds = dh - vdp$$

$$dh = Tds + vdp$$

$$dz = Mdx + Ndy$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial v}{\partial S}\right)_P} \quad -(2)$$

(3)

$$G = H - TS$$

$$dG = dH - Tds - SdT$$

$$Tds = dH - vdP$$

$$dh - Tds = vdP$$

$$dG = vdp - SdT$$

$$dz = Mdx + Ndy$$

$$\boxed{\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \quad -(3)$$

(4)

$$F = U - TS$$

$$dF = dU - Tds - SdT$$

$$Tds = du + Pdv$$

$$du - Tds = -Pdv$$

$$dF = -Pdv - SdT$$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T} \quad -(4)$$

# (T)hermal (P)ower (S)tation in (V)illage

T-2
T-3

$$\begin{array}{c|c} T & P \\ \hline V & S \end{array} \qquad \begin{array}{c|c} T & V \\ \hline P & S \end{array} \qquad \begin{array}{c|c} P & S \\ \hline T & V \end{array} \qquad \begin{array}{c|c} V & S \\ \hline T & P \end{array}$$

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

## T-ds equation:-

### 1st T-ds equation:

$$Tds = du + Pdv$$

$$ds = \frac{du}{T} + \frac{P}{T}\,dv$$

$$du = \frac{C_v\,dT}{T} \qquad pv = RT$$

$$\frac{P}{T} = \frac{R}{V}$$

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

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

use partial diff

$$\partial s = \left(\frac{\partial s}{\partial T}\right)_V dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

Multiple with T

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_V dT + T\left(\frac{\partial s}{\partial v}\right)_T dv \quad -(A)$$

$$\Rightarrow \quad Tds = du + Pdv$$

$$v = c \quad , du = C_v dT$$

$$T\left(\frac{\partial s}{\partial T}\right)_v = C_v \quad -(B)$$

Use max. eqn 4

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

Use (B) & (C) in (A)

$$\boxed{Tds = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv} \quad -(5)$$

## 2nd T-ds equation

$$Tds = dh - vdP$$

$$ds = \frac{dh}{T} - \frac{v}{T} dP$$

$$dh = C_p \cdot dT \quad \& \quad \frac{v}{T} = \frac{R}{P}$$

$$ds = C_p \frac{dT}{T} - R\frac{dP}{P}$$

$$s = f(T, P)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$

Multipli with T

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_P dT + T\left(\frac{\partial s}{\partial P}\right)_T dP \quad -(A)$$

$$Tds = dh - vdP$$

$$P = C$$

$$T\left(\frac{\partial s}{\partial T}\right)_P = C_P \quad \text{—} (B)$$

Use eq$^n$ (3) max

$$\left(\frac{\partial s}{\partial P}\right)_T = \left(\frac{\partial v}{\partial T}\right)_P \quad \text{—} (C)$$

use (B) & (C) in (A)

$$\boxed{Tds = C_P dT - T\left(\frac{\partial v}{\partial T}\right)_P dP} \quad \text{—} (6)$$

Volume expansivity ($\beta$) :-

$$\boxed{\beta = \frac{1}{v}\left(\frac{dv}{dT}\right)_P} \quad \text{—} (7)$$

Isothermal compressibility ($K_T$) :-

It is the reciprocal of Bulk Modulas

Bulk Modulas :- it is defined as the ratio of direct stress to volumetric strain

$$\text{Comp.} = \frac{1}{\text{B.M.}}$$

$$\text{B.M.} = \frac{-dP}{\left(\frac{dv}{v}\right)} = -v\left(\frac{dP}{dv}\right)$$

$$\text{Isothermal Comp.} = \frac{1}{\text{B.M.}} = \frac{-1}{v\left(\frac{dP}{dv}\right)} = -\frac{1}{v}\left(\frac{dv}{dP}\right)_T$$

$$\boxed{K_T = -\frac{1}{v}\left(\frac{dv}{dP}\right)_T} \quad \text{—} (8)$$

Que:- Prove that $C_p - C_v = \frac{T V \beta^2}{k_T}$

Soln Comparing eq ⑤ and ⑥

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

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

$$dT = \frac{T}{C_p - C_v}\left(\frac{\partial P}{\partial T}\right)_V dV + \frac{T}{C_p - C_v}\left(\frac{\partial V}{\partial T}\right)_P dP \quad \text{—(A)}$$

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

use partial diff

$$dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV \quad \text{—(B)}$$

compare (A) & (B)

$$\frac{T}{C_p - C_v}\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial T}{\partial V}\right)_P$$

$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad - (C)$$

use theorem (3)

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

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -1$$

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

use (D) in (C)

$$C_p - C_v = T\left[-\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right] \left(\frac{\partial V}{\partial T}\right)_P$$

$$\boxed{C_p - C_v = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2} \quad - (9)$$

Note Que:- Prove that $C_p$ is always greter then $C_v$

Ans:- The slope of constant temp line on P-V curve is always negative therefore by using eqⁿno (9) we can say that $C_p$ is alway greater the $C_v$

$$PV = C \Rightarrow P \propto \frac{1}{V}$$

$$C_p - C_v = -[(+ve)(-ve)(+ve)]$$

$$C_p - C_v > 0$$

$$\boxed{C_p > C_v}$$

use eq$^n$ No. (7)

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \beta V \quad \text{—(E)}$$

use eq$^n$ No. (8)

$$k_T = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T \Rightarrow \left(\frac{dV}{dP}\right)_T = -k_T V \quad \text{—(F)}$$

use (E) & (F) in eq (9)

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2$$

$$\boxed{C_P - C_V = \frac{TV\beta^2}{k_T}} \quad \text{—— (10)}$$

Joule - Thomson coefficient :—

or Joule - Kelvin effect :—

$$Tds = dh - Vdp$$

$$dh = Tds + Vdp$$

use eq no (6) $\quad Tds = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \quad$ —(6)

$$dh = \left[C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP\right] + Vdp$$

$$dh = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP \quad \text{—(A)}$$

$$dh = 0$$

$$C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP = 0$$

$$C_p dT = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$$

$$\left(\frac{dT}{dP}\right)_h = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

$$\boxed{\mu_J = \left(\frac{dT}{dP}\right)_h = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]} \quad — (11)$$

Note:- The value of Joule Thomson coefficient ($\mu_J$) is zero for an ideal gas.

$$PV = RT$$

Diff

$$P\,dV + \cancel{V\,dP}^{\to 0} = R\,dT + \cancel{T\,dR}^{\to 0}$$

$P = C$

$$\boxed{\left(\frac{dV}{dT}\right)_P = \frac{R}{P}}$$

$$T\left(\frac{dV}{dT}\right)_P = \frac{TR}{P} = V \quad — (13)$$ use in (11)

$\boxed{\mu_J = 0}$ for ideal Gas
$PV = RT$

Question:- Prove that enthalpy is a function of Temp. ~~and~~ only for ideal gas.

Ans using eq$^n$ (A) (Refer $\mu_J$)

$$dh = C_p\, dT + \left[-T\left(\frac{dv}{dT}\right)_p + v\right] dp \quad \text{—(A)}$$

use (B) in (A)

$$T\left(\frac{dv}{dT}\right)_p = \frac{TR}{P} = v$$

$$\boxed{dh = C_p\, dT}$$ for ideal Gas

Question:- Prove that internal energy is a function of Temp only for ideal Gas.

~~use~~ $Tds = du + P\,dv$

use 1$^{st}$ Tds

$$du = C_v\, dT + T\left(\frac{\partial P}{\partial T}\right)_v dv - P\,dv$$

$$du = C_v\, dT + \left[-P + T\left(\frac{\partial P}{\partial T}\right)_v\right] dv \quad \text{—(A)}$$

$$PV = RT$$

$$\cancel{P\,dv} + v\,dP = R\,dT + \cancel{T\,dR}$$

$$v = c \quad \left(\frac{dP}{dT}\right) = \frac{R}{V} \Rightarrow \frac{TR}{V} = P$$

$$v\,dp = R\,dT \Rightarrow \boxed{\left(\frac{dp}{dT}\right)_v = \frac{R}{V}}$$

$$T\left(\frac{dp}{dT}\right)_v = \frac{RT}{V} = P \quad -(B)$$

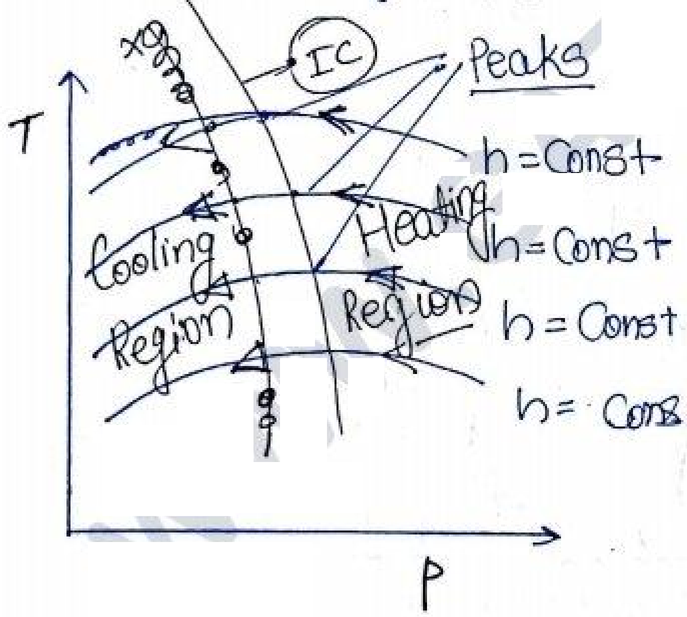
use (B) in (A)

$$\boxed{du = C_v\,dT}$$

Inversion curve :- It is a curve which is generated by Joining the picks of different isenthalpic process on T—P Plot.

☆ outside the inversion curve the region is called as heating region and having −ve slop.

☆ Inside the inversion curve the region is called as cooling region and having +ve slop.

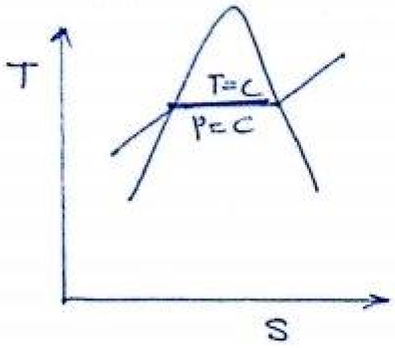




$$\frac{dT}{dp} = \frac{+ve}{-ve} = \underline{-ve}$$


$$\frac{dT}{dp} = \frac{-ve}{-ve} = \underline{+ve}$$

Clapeyron clausius equation :-




In the case of wet Region pressure and temp are independent of Volume

using eq$^n$ (4) $f = U - TS$

$$\left(\frac{dP}{dT}\right)_V = \left(\frac{ds}{dv}\right)_T$$

$$\left(\frac{dP}{dT}\right)_V = \frac{\left(\frac{dQ}{T}\right)}{dv} = \frac{m\,h_{fg}}{T\,dV} = \frac{h_{fg}}{T\,dv}$$

$$\boxed{\left(\frac{dP}{dT}\right)_V = \frac{h_{fg}}{T v_{fg}} = \frac{(h_g - h_f)}{T(v_g - v_f)}} \quad \text{— (12)}$$

$v_g >>> v_f$

$$\therefore \left(\frac{dP}{dT}\right)_V = \left(\frac{LH}{T v_g}\right) \quad \text{— (A)}$$

$PV = mRT$

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

$v = \frac{RT}{P}$ — (B)

use (B) in (A)

$$\boxed{\left(\frac{dP}{dT}\right)_V = \frac{P(LH)}{RT^2}} \quad \text{— (13)}$$

Polio hospital

CH-07

(1)

$$\left(\frac{dP}{dT}\right)_{Sat} = 17.69 \; kPa/K$$

$V_f = 0.0008157 \; m^3/kg$

$V_g = 0.0358 \; m^3/kg.$

$$\left(\frac{dP}{dT}\right)_{Sat} = \frac{\cancel{P(LH)}}{\cancel{RT^2}} = \frac{h_{fg}}{T\,v_{fg}}$$

$$17.69 = \frac{h_{fg}}{(293)(0.0358 - 0.008157)} \qquad \frac{kPa}{K} \times K \times m^3/kg$$

$$h_{fg} = 181.5 \; kJ/kg$$

(2) a, d (3)

$T = 76°C = 349K$

$LH = 195 \; kJ/kg.$

$R = 0.055 \; kJ/kgK$

$P = 202 \; kPa$

$$\left(\frac{dP}{dT}\right)_v = \frac{P(LH)}{RT^2} = \frac{101 \times 195}{0.055 \times (349)^2} = 2.93 \; kJ/kgK$$

$\frac{kJ \times kJ/kg}{kJ} \; \frac{kgK}{K^2}$

$$\frac{101 \times 195}{0.055} = \frac{202 \times 195}{} \left(\frac{dP}{dT}\right)_v =$$

$P \propto T^2$

$$\frac{P_1}{P_2} = \left(\frac{T_1}{T_2}\right)^2$$

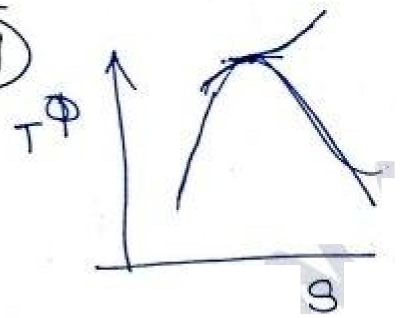
(22)

$$\left(\frac{dP}{dT}\right)_V = \frac{h_{fg}}{T\,v_{fg}}$$

$$31 = \frac{h_{fg}}{473(0.1274 - 0.001157)}$$

$$h_{fg} = 1851.10 \ \mathrm{KJ/kg}.$$

(24)




(17)

$$C_p - C_v = \frac{T V \beta^2}{K_T}$$

$\beta = 5 \times 10^{-3} \ K^{-1}$

$K_t = 8.6 \times 10^{-12} \ m^2/N$

$T = 298 \ K$

$v = 0.000114 \ m^3/kg.$

$$C_p - C_v = \frac{(298)(0.000114)(5 \times 10^{-3})^2}{(8.6 \times 10^{-12})}$$

$$\frac{C_p}{C_v} = 1.024$$

$C_p = 1.024\, C_v$

3

$$\frac{dP}{dT} = \frac{P(LH)}{RT^2}$$

$$\int \frac{dP}{P} = \frac{LH}{R} \int \frac{dT}{T}$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{LH}{R}\left(-\frac{1}{T_2} + \frac{1}{T_1}\right)$$

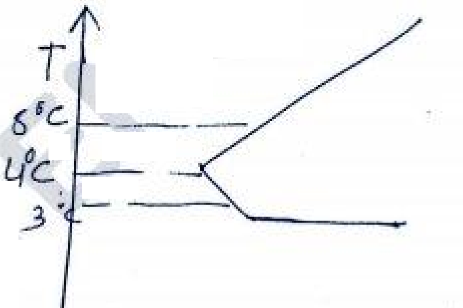
349

$$\ln(2) = \frac{195}{0.055}\left(-\frac{1}{T_2} + \frac{1}{349}\right)$$

$$T_2 = 374.54\,K$$

6

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


$3 \to 4°C$ $\left(\frac{dv}{dt}\right)$ -ve so $\left(\frac{ds}{dp}\right)$ +ve

$4 \to 5$ $\frac{dv}{dt}$ +ve so $\frac{ds}{dp}$ -ve

7

$$\ln P_{sat} = A - \frac{B}{T_{sat}}$$

$$\left(\frac{dP}{dT}\right) = \frac{h_{fg}}{T v_{fg}}.$$

$$\frac{1}{P_{sat}} \frac{dP_{sa}}{dt} = 0 + \frac{B}{T_{sat}^2}$$

$$\frac{dP}{dt} = \frac{P_{sat} B}{T_{sat}} = \frac{h_{fg}}{T V_{fg}}$$

$$h_{fg} = \frac{P_{sa} V_{fg} B}{T_{sat}}$$