

## Maxwell's Thermodynamical Relationship

from the 1<sup>st</sup> law of thermodynamics, Maxwell derived 6 fundamental thermodynamic relations using P, V, T, S with any two pair as dependent & other as independent variable.

From 1<sup>st</sup> law,  $dQ = dU + PdV$  & from 2<sup>nd</sup> law,  $dS = Tds$

$$\therefore dU = dQ - PdV = Tds - PdV \quad \text{--- (1)}$$

Here  $dU, ds, dV$  are all exact differentials. Considering U, S, V as function of two independent variables  $x$  &  $y$  where  $\{x, y\} = \{\text{combination of } P, V, T, S \text{ any two}\}$ . Then,

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

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

$$\begin{aligned} \text{Substituting in (1), } \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy &= T \left[ \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \right] \\ &\quad - P \left[ \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \right] \\ &= \left[ T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial y}\right)_x \right] dx + \left[ T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial x}\right)_y \right] dy \end{aligned}$$

Comparing the coefficients of  $dx$  &  $dy$ , we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial y}\right)_x, \quad \left(\frac{\partial U}{\partial y}\right)_x = T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial x}\right)_y$$

Since  $dU$  is a perfect differential,  $\frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x}$ , so

$$\left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x + T \cancel{\frac{\partial^2 S}{\partial x \partial y}} - P \cancel{\frac{\partial^2 V}{\partial x \partial y}} = 0$$

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y + T \cancel{\frac{\partial^2 S}{\partial y \partial x}} - P \cancel{\frac{\partial^2 V}{\partial y \partial x}} = 0$$

$$\therefore \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y = \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y$$

This is the general expression for Maxwell's T.D. relation, which can be written in determinant form

$$\begin{vmatrix} \left(\frac{\partial T}{\partial x}\right)_y & \left(\frac{\partial T}{\partial y}\right)_x \\ \left(\frac{\partial S}{\partial x}\right)_y & \left(\frac{\partial S}{\partial y}\right)_x \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial x}\right)_y & \left(\frac{\partial P}{\partial y}\right)_x \\ \left(\frac{\partial V}{\partial x}\right)_y & \left(\frac{\partial V}{\partial y}\right)_x \end{vmatrix}$$

or, 
$$\frac{\partial(T, S)}{\partial(x, y)} = \frac{\partial(P, V)}{\partial(x, y)}$$

There are  ${}^4C_2 = 6$  combinations  $(S, V)$ ,  $(T, V)$ ,  $(S, P)$ ,  $(T, P)$ ,  $(P, V)$ ,  $(T, S)$ .

1<sup>st</sup> Relation: Let  $x = S$ ,  $y = V$ , then we have

$$\begin{vmatrix} 1 & 0 \\ \left(\frac{\partial S}{\partial T}\right)_V & \left(\frac{\partial S}{\partial V}\right)_T \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial T}\right)_V & \left(\frac{\partial P}{\partial V}\right)_T \\ 0 & 1 \end{vmatrix} \quad \text{or} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

So the first relation says, increase of entropy per unit increase of volume at constant temperature is equal to the increase of pressure per unit increase of temperature when the volume is kept constant.

2<sup>nd</sup> Relation: Let  $x = T$ ,  $y = P$ , then we have

$$\begin{vmatrix} 1 & 0 \\ \left(\frac{\partial S}{\partial T}\right)_P & \left(\frac{\partial S}{\partial P}\right)_T \end{vmatrix} = \begin{vmatrix} 0 & 1 \\ \left(\frac{\partial V}{\partial T}\right)_P & \left(\frac{\partial V}{\partial P}\right)_T \end{vmatrix} \quad \text{or} \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

This means decrease of entropy per unit increase of pressure during an isothermal transformation is equal to the increase in volume per unit increase in temperature when the pressure remains constant.

3<sup>rd</sup> Relation: Let  $x=S$ ,  $y=V$ ,  $\begin{vmatrix} \left(\frac{\partial T}{\partial S}\right)_V & \left(\frac{\partial T}{\partial V}\right)_S \\ 1 & 0 \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial S}\right)_V & \left(\frac{\partial P}{\partial V}\right)_S \\ 0 & 1 \end{vmatrix}$

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

4<sup>th</sup> Relation: Let  $x=S$ ,  $y=P$ ,  $\begin{vmatrix} \left(\frac{\partial T}{\partial S}\right)_P & \left(\frac{\partial T}{\partial P}\right)_S \\ 1 & 0 \end{vmatrix} = \begin{vmatrix} 0 & 1 \\ \left(\frac{\partial V}{\partial S}\right)_P & \left(\frac{\partial V}{\partial P}\right)_S \end{vmatrix}$

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

5<sup>th</sup> Relation: Let  $x=P$ ,  $y=V$ ,  $\begin{vmatrix} \left(\frac{\partial T}{\partial P}\right)_V & \left(\frac{\partial T}{\partial V}\right)_P \\ \left(\frac{\partial S}{\partial P}\right)_V & \left(\frac{\partial S}{\partial V}\right)_P \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$

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

6<sup>th</sup> Relation: Let  $x=T$ ,  $y=S$ ,  $\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial T}\right)_S & \left(\frac{\partial P}{\partial S}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_S & \left(\frac{\partial V}{\partial S}\right)_T \end{vmatrix}$

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

### Applications of Maxwell's Thermodynamic Relations

from the relation  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$  after multiplying by  $T$  we

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

$\left(\frac{\partial Q}{\partial V}\right)_T$  represents heat absorbed or liberated per unit change in volume at constant temperature. This heat represents latent heat when substance changes from solid to liquid (melting) or liquid to vapour (boiling) state at constant temperature. If  $L$  is the heat required to change unit mass of substance,  $V_2$  &  $V_1$  be specific volume (volume per unit mass) then  $\left(\frac{\partial Q}{\partial V}\right)_T = \frac{L}{V_2 - V_1}$

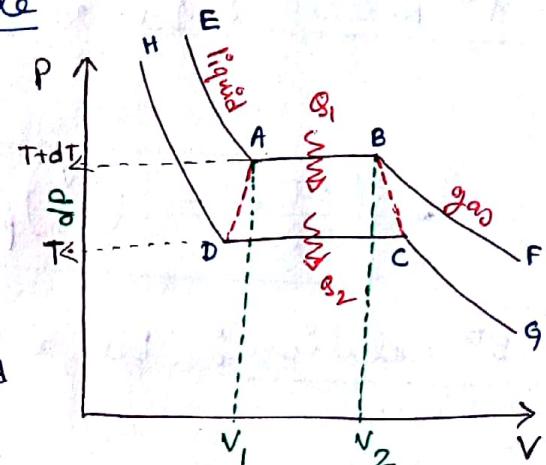
$$\therefore \frac{L}{V_2 - V_1} = T \left( \frac{\partial P}{\partial T} \right)_V$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

Clausius-Clapeyron's latent heat equation.

### Latent heat equation using Carnot's cycle

Consider two isothermals FBAE and GCDH with a cycle ABCD where Carnot's theorem can be applied. At point A, volume is  $V_1$  & temperature  $T+dT$  & pressure is just below its saturation pressure & liquid begins to evaporate till point B at volume  $V_2$  where it's in the vapour state. If mass of liquid at B is 1 gm, the amount of heat absorbed is  $Q_1 = L + dL$  is latent heat at  $T+dT$ .



At B, pressure decreases by  $dP$  & vapour expands & temperature falls to point C at temperature T. Here the gas starts to condense & changes to liquid state at point D. The amount of heat rejected for  $C \rightarrow D$  is  $L = Q_2$ . Increasing the pressure, reversibly A point is restored.

$$\text{From Carnot's theorem, } \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \Rightarrow \frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2}$$

Here  $Q_1 - Q_2 = dL$ ,  $T_1 - T_2 = dT$ ,  $Q_2 = L$ ,  $T_2 = T$ .

$$\therefore \frac{dL}{L} = \frac{dT}{T}. \text{ Now } dL = Q_1 - Q_2 = dP(V_2 - V_1) = \text{area of } ABCD$$

$$\therefore \frac{dP(V_2 - V_1)}{L} = \frac{dT}{T} \quad \text{in} \quad \boxed{\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}}.$$

Using this, let's calculate the change in freezing point of a substance by pressure. Consider the melting of ice to water at  $0^\circ\text{C}$ , where  $T = 273.16\text{K}$  &  $L = 99.6 \times 4.2 \times 10^9 \text{ Ergs}$ ,  $V_2$  = volume of unit mass of water =  $1.0001 \text{ cc}$  &  $V_1$  = volume of unit mass of ice =  $1.0908 \text{ cc}$

$$\therefore \left( \frac{dp}{dT} \right)_{\text{Saturation}} = \frac{99.6 \times 4.2 \times 10^7}{273.16 \times (1.0001 - 1.0908)} . \quad \text{If } dp = 1 \text{ atm} \\ = 1.01 \times 10^6 \text{ dynes/cm}^2$$

then we obtain  $dT = -0.0075^\circ\text{C}$ .  $\therefore$  To reduce  $1^\circ\text{C}$  temperature of the melting point of ice, one has to apply  $\Delta p = \frac{1}{0.0075} \approx 133 \text{ atm}$  of pressure.

Consider the other extreme i.e. boiling point of water at  $100^\circ\text{C}$  when  $L = 537.6 \times 1.2 \times 10^7 \text{ ergs}$ ,  $V_1 = 1.0001 \text{ cc} \& V_2 = 1674 \text{ cc}$ .

In this case,  $\frac{dp}{dT} > 0$  meaning there will be an increase in boiling point if the pressure on the water is increased.

$\therefore$  Ice will melt at lower than  $0^\circ\text{C}$  at a higher pressure than 76 cm of Hg. Also water will boil at a lower temperature under reduced pressure or boiling point increases with increase in pressure.

### Adiabatic Stretching of wire using Maxwell's relations

from 1<sup>st</sup> & 2<sup>nd</sup> law, using  $dS = dU + PdV$ , we have

$TdS = dU + PdV$ . In case of stretching a wire,  $dW = -\vec{F} \cdot d\vec{l}$

$$\therefore dU = TdS + Fdl \quad \begin{matrix} P \leftrightarrow -F \\ V \leftrightarrow l \end{matrix} \quad \text{replacement.}$$

$$\text{we get from } \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V, \quad \left( \frac{\partial T}{\partial l} \right)_S = \left( \frac{\partial F}{\partial S} \right)_V = T \left( \frac{\partial F}{\partial S} \right)_V \\ = T \left( \frac{\partial F}{\partial \dot{S}} \right)_V$$

$$\therefore \left( \frac{\partial T}{\partial l} \right)_S = T \left( \frac{\partial F}{\partial T} \right)_F \left( \frac{\partial T}{\partial \dot{S}} \right)_F \quad \dots \text{①}$$

$$\text{Now } l = l(F, T) \quad \therefore dl = \left( \frac{\partial l}{\partial F} \right)_T df + \left( \frac{\partial l}{\partial T} \right)_F dT$$

$$\text{Under no elongation } dl = 0, \quad 0 = \left( \frac{\partial l}{\partial F} \right)_T df + \left( \frac{\partial l}{\partial T} \right)_F dT$$

$$\therefore \left( \frac{\partial F}{\partial T} \right)_F = - \frac{\left( \frac{\partial l}{\partial T} \right)_F}{\left( \frac{\partial l}{\partial F} \right)_T}$$

$$\text{Substituting this in equation ①, we get } \left( \frac{\partial T}{\partial l} \right)_S = -T \frac{\left( \frac{\partial l}{\partial T} \right)_F}{\left( \frac{\partial l}{\partial F} \right)_T} \left( \frac{\partial T}{\partial \dot{S}} \right)_V$$

Coefficient of linear expansion  $\beta = \frac{1}{l} \left( \frac{\partial l}{\partial T} \right)_F$

Isothermal Young's modulus  $Y_T = \frac{l}{A} \left( \frac{\partial F}{\partial l} \right)_T$

Specific heat at constant length  $c_e = \left( \frac{\partial S}{\partial T} \right)_e$

$$\therefore \left( \frac{\partial T}{\partial l} \right)_S = - T \frac{\beta l}{\left( \frac{l}{Y_T A} \right)} \frac{1}{c_e} = - \frac{T \beta Y_T A}{mc}, \quad m = \text{mass/unit length}$$

$c = \text{sp. heat of wire}$

Using  $Y_s = \frac{l}{A} \left( \frac{\partial F}{\partial l} \right)_S$ , we have  $\left( \frac{\partial T}{\partial F} \right)_S = \left( \frac{\partial T}{\partial l} \right)_S \left( \frac{\partial l}{\partial F} \right)_S$

$$= - \frac{T \beta Y_T A}{mc} \frac{1}{Y_S A} \approx - \frac{T \beta}{mc}$$

$$\therefore dT = - \frac{T \beta}{mc} dF \quad (Y_T \approx Y_s)$$

for solids

If  $\beta > 0$ , then increase in tension should cool the wire. for an adiabatic stretching.

Adiabatic stretching of a liquid film using Maxwell's relations

$$dQ = dU + dW \quad (\text{1st law}) \quad \text{yields} \quad dU = dQ - dW \\ = dQ + 2\gamma dA$$

where  $-2\gamma dA$  is the work done by the surface film with surface tension  $\gamma$ . Comparing with  $PdV$ ,  $P \leftrightarrow -2\gamma$   
 $V \leftrightarrow A$

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

$$\therefore \left( \frac{\partial S}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V. \quad \text{Substituting, } \left( \frac{\partial S}{\partial A} \right)_T = -2T \left( \frac{\partial \gamma}{\partial T} \right)_A$$

$\therefore$  for a finite change of area  $dA$  we have

$$dQ = -2T \left( \frac{\partial \gamma}{\partial T} \right)_A dA. \quad \text{for a liquid, surface tension decreases}$$

with temperature so  $\left( \frac{\partial \gamma}{\partial T} \right)_A < 0$ , or  $d\gamma > 0$ .  $\therefore$  To keep temperature constant of the film,  $dQ$  amount of heat is to be supplied when stretch

In adiabatic stretching, the fall in temperature is

$$\Delta T = \frac{c}{C} \left( \frac{\partial S}{\partial T} \right)_A dA \quad \text{where } C \text{ is the heat capacity for the liquid film}$$

### Clausius latent heat equation.

for a change of state from liquid to vapour,  $S_v - S_l = \frac{L}{T}$ . Differentiating with respect to  $T$ , we have

$$\frac{dS_v}{dT} - \frac{dS_l}{dT} = -\frac{L}{T^2} + \frac{L}{T} \frac{dL}{dT}$$

$$\therefore T \left( \frac{dS_v}{dT} \right) - T \left( \frac{dS_l}{dT} \right) = -\frac{L}{T} + \frac{dL}{dT}$$

$$\therefore C_v - C_l = \frac{dL}{dT} - \frac{L}{T} \quad *(\text{see page 10})$$

### More applications of Maxwell's relations

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

$$\therefore \left( \frac{\partial S}{\partial P} \right)_T = -T \left( \frac{\partial V}{\partial T} \right)_P. \quad \text{But the coefficient of volume}$$

$$\text{expansion } \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \therefore \left( \frac{\partial V}{\partial T} \right)_P = V\alpha.$$

$$\therefore \left( \frac{\partial S}{\partial P} \right)_T = -TV\alpha. \quad \text{If } \alpha > 0 \text{ or if the substance expands on heating then } \left( \frac{\partial S}{\partial P} \right)_T < 0, \text{ meaning heat must be withdrawn}$$

from the substance to keep temperature constant when the pressure is increased. On other hand if  $\alpha < 0$ , the substance contracts on heating,  $\left( \frac{\partial S}{\partial P} \right)_T > 0$  meaning heat must be added to keep its temperature constant, when the pressure is increased.

|| Increase in pressure heats a body that expands on rise of temperature. Cooling is produced when a substance, which contracts on heating, is suddenly compressed.

## Energy Equations of Pure Substances

From first law of T.D.  $dU = TdS - PdV$  — ①

Using Maxwell's relation  $(\frac{\partial U}{\partial V})_T = T(\frac{\partial S}{\partial V})_T - P$ .

$$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V, \quad (\frac{\partial U}{\partial V})_T = T(\frac{\partial P}{\partial T})_V - P$$

*1st Energy equation*

For Ideal Gas

$$PV = nRT \quad \therefore (\frac{\partial P}{\partial T})_V = \frac{nR}{V}$$

$\therefore$  from energy equation,  $(\frac{\partial U}{\partial V})_T = T \frac{nR}{V} - P = 0$ . So  $U$  is a function  $T$  only and does not depend on  $V$ .

For Van der Waals Gas

$$(P + \frac{a}{v^2})(v-b) = RT$$

$$\therefore P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\therefore (\frac{\partial P}{\partial T})_V = \frac{R}{v-b} \quad \therefore \text{Using 1st Energy equation}$$

$$(\frac{\partial U}{\partial V})_T = \frac{RT}{v-b} - P = \frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2} = \frac{a}{v^2}$$

$$\therefore dU = C_V dT + \frac{a}{v^2} dv \quad \therefore U = \int C_V dT - \frac{a}{v} + \text{const.}$$

So the internal energy increases with increasing volume at constant temperature.

Again, using ①,  $(\frac{\partial U}{\partial P})_T = T(\frac{\partial S}{\partial P})_T - P(\frac{\partial V}{\partial P})_T$ .

Using Maxwell's relation,  $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$  we obtain

$$(\frac{\partial U}{\partial P})_T = -T(\frac{\partial V}{\partial T})_P - P(\frac{\partial V}{\partial P})_T$$

*2nd Energy equation*

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Using equation of state  $f(p, v, T) = 0$ ,  $df = 0$

$$\Rightarrow \left(\frac{\partial f}{\partial p}\right) dp + \left(\frac{\partial f}{\partial v}\right) dv + \left(\frac{\partial f}{\partial T}\right) dT = 0.$$

for isobaric process,  $\left(\frac{\partial f}{\partial v}\right) dv = -\left(\frac{\partial f}{\partial T}\right) dT$   $\Rightarrow \left(\frac{\partial v}{\partial T}\right)_p = -\frac{\left(\frac{\partial f}{\partial T}\right)}{\left(\frac{\partial f}{\partial v}\right)}$

for isochoric process,  $\left(\frac{\partial f}{\partial p}\right) dp = -\left(\frac{\partial f}{\partial T}\right) dT$   $\Rightarrow \left(\frac{\partial p}{\partial T}\right)_v = -\frac{\left(\frac{\partial f}{\partial T}\right)}{\left(\frac{\partial f}{\partial p}\right)}$

for isothermal process,  $\left(\frac{\partial f}{\partial p}\right) dp = -\left(\frac{\partial f}{\partial v}\right) dv$ ,  $\Rightarrow \left(\frac{\partial p}{\partial v}\right)_T = -\frac{\left(\frac{\partial f}{\partial v}\right)}{\left(\frac{\partial f}{\partial p}\right)}$

$$\therefore \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v = -1.$$

Using this, we can recompute 1<sup>st</sup> energy equation as

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p = \left[-v \left(\frac{\partial p}{\partial v}\right)_T\right] \left[\frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p\right] = \frac{\beta}{K}$$

where  $K_p$  = isothermal compressibility &  $\beta$  = volume expansivity.

$$\therefore \boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{T\beta}{K} - p}$$

$\left(\frac{\partial U}{\partial V}\right)_T$  is known as "internal pressure" that arises due to the intermolecular attraction. Fact that gases condense to form liquid & solids shows that there exist intermolecular attraction that pulls the gas atoms together even without any external pressure. When the temperature is increased, the pressure diminishes till it becomes zero at the perfect gas stage.

T-dS Equations Entropy of a pure substance is

$$S = S(T, V) \quad \Rightarrow \quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\therefore TdS = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$= \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

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

$$\boxed{TdS = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV}$$

1<sup>st</sup> T-dS Equation

$$\text{Similarly, } S = S(T, P), \quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

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

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

or  $TdS = C_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP$  2<sup>nd</sup> T-dS Equation

Equating the first & second T-dS equation, we obtain

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

$$\text{or } (C_P - C_V) dT = T \left(\frac{\partial V}{\partial T}\right)_P dP + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\text{or, } dT = \frac{T \left(\frac{\partial V}{\partial T}\right)_P dP}{C_P - C_V} + \frac{T \left(\frac{\partial P}{\partial T}\right)_V dV}{C_P - C_V}$$

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

$$\therefore \text{Equating the coefficients, we get, } \left(\frac{\partial T}{\partial P}\right)_V = \frac{T \left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_V}$$

$$\text{or } C_P - C_V = T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

$$\text{Using } \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1, \text{ we have } C_P - C_V = -T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

$$= TV \left[ \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \right]^2 \left[ -V \left(\frac{\partial P}{\partial V}\right)_T \right] = \frac{TV\beta^2}{K_T}$$

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

This is one of the important equations of Thermodynamics which shows that **(a)** As  $\left(\frac{\partial P}{\partial V}\right)_T < 0$  always for most substances, therefore  $C_P - C_V > 0$  or  $C_P > C_V$ . **(b)** As  $T \rightarrow 0$ ,  $C_P \rightarrow C_V$  or at absolute zero the two heat capacities are equal. **(c)** When  $\left(\frac{\partial V}{\partial T}\right)_P = 0$ , we obtain  $C_P = C_V$ . Water at  $4^\circ\text{C}$  have maximum density & minimum volume so that heat capacities become equal.

If  $K_s = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S$  and  $K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_T$  then using 1<sup>st</sup> & 2<sup>nd</sup> T-ds equation at constant S, we have

$$TdS = 0 = Cp dT_S - T \left( \frac{\partial V}{\partial T} \right)_P dP_S \quad \Rightarrow \quad Cp dT_S = T \left( \frac{\partial V}{\partial T} \right)_P dP_S$$

$$TdS = 0 = C_V dT_S + T \left( \frac{\partial P}{\partial T} \right)_V dV_S \quad \Rightarrow \quad C_V dT_S = -T \left( \frac{\partial P}{\partial T} \right)_V dV_S$$

$$\therefore \frac{C_P}{C_V} = \gamma = -\frac{\left( \frac{\partial V}{\partial T} \right)_P}{\left( \frac{\partial P}{\partial T} \right)_V} \frac{\left( \frac{\partial P}{\partial V} \right)_S}{\left( \frac{\partial V}{\partial P} \right)_T} = +\frac{\left( \frac{\partial P}{\partial V} \right)_S}{\left( \frac{\partial P}{\partial V} \right)_T} = \frac{-\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S}{-\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T} = \frac{K_S}{K_T}$$

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

$$\therefore \boxed{\gamma = \frac{C_P}{C_V} = \frac{K_S}{K_T}} = \frac{\text{adiabatic compressibility}}{\text{isothermal compressibility}}$$

HW ① Consider a metal (say Copper) at 300K with the following values,  $V = 7.06 \text{ cm}^3/\text{mol}$ ,  $K_T = 7.78 \times 10^{-12} \text{ N/m}^2$ ,  $\beta = 50.4 \times 10^{-6} \text{ K}^{-1}$ ,  $C_P = 24.5 \text{ J/mol K}$ . Determine  $C_V$ .

② Prove that ratio of adiabatic ( $\alpha_s = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_S$ ) to isobaric ( $\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$ ) coefficient of expansion is  $\frac{1}{1-\gamma}$ . Also prove that

adiabatic ( $E_s = -V \left( \frac{\partial P}{\partial V} \right)_S$ ) to isothermal ( $E_T = -V \left( \frac{\partial P}{\partial V} \right)_T$ ) elasticities is equal to ratio of specific heats.

③ Prove that adiabatic ( $\beta_s = \frac{1}{P} \left( \frac{\partial P}{\partial T} \right)_S$ ) to isochoric ( $\beta_v = \frac{1}{P} \left( \frac{\partial P}{\partial T} \right)_V$ ) pressure coefficient of expansion is  $\frac{\gamma}{\gamma-1}$ .

Variation of  $C_V$  with  $V$  and  $C_P$  with  $P$

From 1<sup>st</sup> T-ds equation,  $dS = \frac{C_V dT}{T} + \left( \frac{\partial P}{\partial T} \right)_V dV$

As  $dS$  is a perfect differential,  $\frac{\partial}{\partial V} \left( \frac{C_V}{T} \right) = \frac{\partial}{\partial T} \left( \frac{\partial P}{\partial T} \right)_V$

$\therefore \frac{\partial C_V}{\partial V} = T \left( \frac{\partial^2 P}{\partial T^2} \right)_V$ . If  $\left( \frac{\partial P}{\partial T} \right)_V = 0$  then  $C_V$  is independent of volume (initial).

Similarly from the 2<sup>nd</sup> Tds equation  $ds = \frac{C_p dT}{T} - \left(\frac{\partial V}{\partial T}\right)_p dP$   
 & ds being exact differential,  $\frac{\partial}{\partial P} \left( \frac{C_p}{T} \right) = - \frac{\partial}{\partial T} \left( \frac{\partial V}{\partial T} \right)_p$   
 $\Rightarrow \frac{\partial C_p}{\partial P} = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_p$

### Negative specific heat of Steam \*

Clausius latent heat equation between two arbitrary states 1 & 2 :-  
 $c_2 - c_1 = \frac{dL}{dT} - \frac{L}{T}$  where  $c$  is the specific heat of substance  
 in states 1 and 2 which is neither at constant volume nor at constant  
 pressure. The vapour always remain in equilibrium with the evaporating  
 liquid, so vapour is in saturated state called "specific heat of saturated  
vapour." From  $S = S(T, P)$ ,  $ds = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$   
 $\Rightarrow \left(\frac{\partial S}{\partial T}\right)_{\text{saturation}} = \left(\frac{\partial S}{\partial T}\right)_P + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{\text{saturation}}$

Using Clausius- Clapeyron latent heat equation,  $\left(\frac{\partial P}{\partial T}\right)_{\text{saturation}} = \frac{L}{T(V_2 - V_1)}$   
 and Maxwell's relation  $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ , we obtain

$$\left(\frac{\partial S}{\partial T}\right)_{\text{saturation}} = \left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial V}{\partial T}\right)_P \frac{L}{T(V_2 - V_1)}$$

$$\therefore c_s = C_p - \left(\frac{\partial V}{\partial T}\right)_P \frac{L}{T(V_2 - V_1)}$$

for evaporation of water at 100°C,  $V_1 = 1 \text{ cc}$ ,  $V_2 = 1674 \text{ cc}$ ,  $L = 537.5 \text{ cal}$   
 $C_p = 0.47$ ,  $\left(\frac{\partial V}{\partial T}\right)_P = 4.813$  gives  $c_s = -1.07 \text{ cal/K}$ . Thus the specific  
 heat of saturated water vapour at 100°C is negative. Though its a  
 paradoxical result but it holds true because specific heat may vary  
 from  $+\infty$  to  $-\infty$  depending on external condition, which is saturation here.  
 Saturated water vapour exerts pressure of 760 mm of Hg at 100°C  
 787.6 mm of Hg at 101°C. i.e. the specific volume of saturated water  
 vapour at 100°C decreases with increasing temperature. When heated,

to  $10^{\circ}\text{C}$  at constant pressure, vapour becomes unsaturated & to satisfy the condition of saturation it is to be compressed till the pressure becomes 787.6 mm. The compression generated heat is large that has to be extracted out to keep the temperature fixed at  $10^{\circ}\text{C}$ . Thus the specific heat of saturated vapour sometimes become negative.

### Properties of van der Waals gas

W equation of state  $(P + \frac{a}{V^2})(V - b) = RT$ .

Using T-ds equation & exact differentiability of S we know

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

$$\text{Now } P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}, \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

$$\therefore \left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

$\therefore C_V$  is independent of volume for VW gas & function of temperature only.

To calculate the variation of entropy of VW gas use T-ds equation

$$dS = \frac{C_V dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV = \frac{C_V}{T} dT + \frac{R}{V-b} dV$$

$$\therefore S = C_V \ln T + R \ln(V-b) + S_0 = \text{constant for adiabatic process}$$

$$\therefore \ln T^{C_V} + \ln(V-b)^R = \text{constant}$$

$$\therefore \ln T^{C_V} (V-b)^{C_P-C_V} = \text{const.} \quad \text{or} \quad T(V-b)^{\frac{C_P-C_V}{C_V}} = \text{constant}$$

$$\boxed{\therefore T(V-b)^{\frac{C_P-C_V}{C_V}-1} = \text{constant}}$$

To calculate the change in internal energy  $U = U(V, T)$

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

$$= C_V dT + \left( \frac{RT}{V-b} - P \right) dV$$

$$= C_V dT + \frac{a}{V^2} dV$$

$$P + \alpha_{V^2} = \frac{RT}{V-b}$$

$$\text{or, } \frac{RT}{V-b} - P = \alpha_{V^2}$$

$$\text{or } \boxed{U = \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2} \frac{a}{V^2} dV = C_V(T_2 - T_1) + a \left( \frac{1}{V_1} - \frac{1}{V_2} \right)}$$

So internal energy of a VW gas depends on the VW pressure coefficient "a" and not on volume coefficient "b". This is because "a" is a measure of the force of attraction between the molecules (Potential energy) that changes as the specific volume of the gas changes & the intermolecular separation changes. "b" is proportional to volume occupied by molecules & it affects the entropy because entropy is volume dependent & occupation of molecules of container volume makes the available volume less than the volume of the container.

$$\text{finally let's calculate } C_p - C_v = TV\beta/k_T = -T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial V} \right)_T$$

$$\text{Now } (P + \frac{a}{V^2})(V-b) = RT \Rightarrow \left( \frac{\partial V}{\partial T} \right)_P (P + \frac{a}{V^2}) + (V-b)(-\frac{2a}{V^3}) \left( \frac{\partial V}{\partial T} \right)_P = R$$

$$\therefore \left( \frac{\partial V}{\partial T} \right)_P \left[ P + \frac{a}{V^2} - \frac{2a}{V^3}(V-b) \right] = R$$

$$\text{or } \left( \frac{\partial V}{\partial T} \right)_P = \frac{R}{\frac{RT}{V-b} - \frac{2a}{V^3}(V-b)} = \frac{R}{\frac{RT}{V-b} \left[ 1 - \frac{2a}{RTV^3}(V-b)^2 \right]}$$

$$\text{Now from } P = \frac{RT}{V-b} - \frac{a}{V^2}, \quad \left( \frac{\partial P}{\partial V} \right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$= -\frac{RT}{(V-b)^2} \left[ 1 - \frac{2a(V-b)^2}{RTV^3} \right]$$

$$\therefore C_p - C_v = T \frac{R^2}{\left( \frac{RT}{V-b} \right)^2 \left[ 1 - \frac{2a}{RTV^3}(V-b)^2 \right]^2} \frac{RT}{(V-b)^2} \left[ 1 - \frac{2a(V-b)^2}{RTV^3} \right]$$

$$= \frac{R}{1 - \frac{2aV^2}{RTV^3} (1 - \frac{b}{V})^2} \underset{\text{as } \frac{b}{V} \ll 1}{\approx} \frac{R}{1 - \frac{2a}{RTV}} \quad [ \text{as } \frac{b}{V} \ll 1 ]$$

$$= R \left( 1 - \frac{2a}{RTV} \right)^{-1} \underset{\text{as } \frac{2a}{RTV} \ll 1}{\approx} R \left( 1 + \frac{2a}{RTV} \right) \quad [ \text{as } \frac{2a}{RTV} \ll 1 ]$$

$$\therefore C_p - C_v = R \left( 1 + \frac{2a}{RTV} \right)$$

Finally work done by VW gas,  $W = - \int P dV = - \int_{V_1}^{V_2} \frac{RT}{V-b} dV + \int_{V_1}^{V_2} \frac{a}{V^2} dV$

$$W = a \left( \frac{1}{V_1} - \frac{1}{V_2} \right) - RT \ln \left[ \frac{V_2-b}{V_1-b} \right]$$