

Maxwell's Thermodynamical Relationship

from the 1st 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 1st law, $dQ = dU + PdV$ & from 2nd 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) .

1st 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.

2nd 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.

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

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

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

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

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

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

6th 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 $\left(\frac{\partial Q}{\partial V}\right)_T = \frac{L}{V_2 - V_1}$

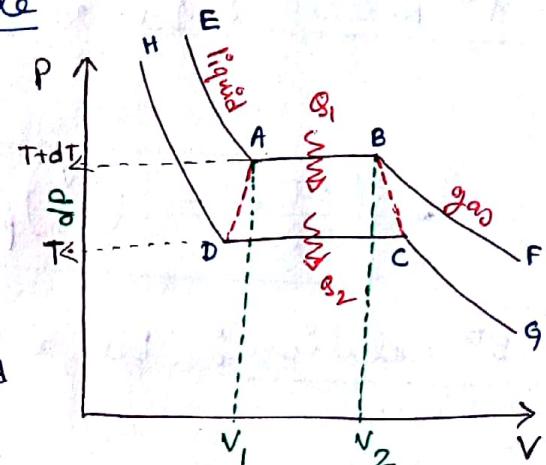
$$\therefore \frac{L}{V_2 - V_1} = T \left(\frac{\partial P}{\partial T} \right)_V$$

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

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°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 cc & V_1 = volume of unit mass of ice = 1.0908 cc

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

then we obtain $dT = -0.0075^\circ\text{C}$. \therefore To reduce 1°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°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°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 1st & 2nd 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 γ . 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

8

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 1st 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 & β = 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

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

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

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

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

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

1st 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 $TdS = C_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP$ 2nd 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°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 1st & 2nd 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 ($\beta_s = \frac{1}{V} \left(\frac{\partial P}{\partial T} \right)_S$) to isochoric ($\beta_v = \frac{1}{V} \left(\frac{\partial P}{\partial T} \right)_V$) pressure coefficient of expansion is $\frac{\gamma}{\gamma-1}$.

Variation of C_V with V and C_P with P

From 1st 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 2nd 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°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°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, $W = - \int P dV = - \int_{V_1}^{V_2} \frac{RT}{V-b} dV + \int_{V_1}^{V_2} \frac{a}{V^2} dV$

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

Liquefaction of Gases

Different methods of liquefaction of gases : (a) Method of freezing mixture, (b) Adiabatic expansion of gas, (c) Joule-Thomson expansion, (d) Throttling process & regenerative cooling, (e) Adiabatic expansion of paramagnetic salt. Adding salt to ice is the well known example of method (a) thereby reducing temperature (eutectic temperature) significantly.

Enthalpy It has been found that a term $U + PV$ appears several times in describing various properties of gas, that is termed as Enthalpy $H = U + PV$. To study its properties, consider change in enthalpy for an infinitesimal process from initial to final equilibrium state,

$$dH = dU + PdV + VdP. \quad \text{But from 1st law of thermodynamics,}$$

$$dQ = dU + dW = dU + PdV. \quad \therefore dH = dQ + VdP.$$

$$\text{At constant pressure, } \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P + V \left(\frac{\partial P}{\partial T}\right)_P = C_P$$

Since $dH = dQ + VdP$, the change in enthalpy during an isobaric process is equal to the heat transferred, so the latent heat measured during a phase transition at constant pressure (e.g. melting, boiling, sublimation) is the change in enthalpy.

$$\therefore H_f - H_i = Q = \int_i^f C_P dT.$$

Isobaric processes are more important than isochoric process in science & technology, so enthalpy plays important role.

from $dH = TdS + VdP$, $\left(\frac{\partial H}{\partial S}\right)_P = T$, $\left(\frac{\partial H}{\partial P}\right)_S = V$. So on a three dimensional diagram $H = H(S, P)$, slopes of the tangent to the surface at a point determines (T, V) .

Throttling process

Suppose a cylinder (thermally insulated) with two nonconducting pistons at two sides of a porous wall contains a gas. The wall (horizontal green lines) is a porous plug made of small holes on a narrow constriction. Initially the gas is at (P_i, V_i) with right hand piston against the wall to prevent seeping of gas, retaining equilibrium. If we now move both pistons simultaneously so that constant pressure P_i (left side of wall) and constant lower pressure P_f (right side of wall) then in final equilibrium state, all gas is sipped to the right side of wall. This is called a "throttling process".

Though it's a nonequilibrium process but initial & final equilibrium states can be described, by applying 1st law

$$\delta = U_f - U_i - W.$$

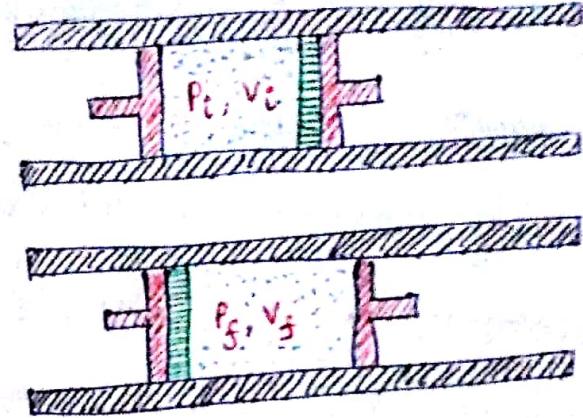
$$\text{No heat transfer happens, so } \delta = 0 \text{ and } W = - \int_0^{V_f} P_f dV - \int_{V_i}^0 P_i dV.$$

$$(\text{as pressure remains constant}) = -P_f V_f + P_i V_i$$

$$\therefore 0 = U_f - U_i + P_f V_f - P_i V_i$$

$$\therefore U_i + P_i V_i = U_f + P_f V_f \quad \boxed{H_i = H_f}$$

So in a throttling process, final & initial enthalpies are equal although intermediate nonequilibrium states cannot have any information about enthalpy & thus cannot be plotted in an indicator diagram as continuous lines/surfaces, but points.



Comparison of Internal Energy U & Enthalpy H

<u>Internal Energy (U)</u>	<u>Enthalpy (H)</u>
# $dU = \delta Q - PdV$, $\left(\frac{\partial U}{\partial T}\right)_V = C_V$	# $dH = \delta Q + VdP$, $\left(\frac{\partial H}{\partial T}\right)_P = C_P$
# Isochoric process $U_f - U_i = Q = \int_i^f C_V dT$	# Isobaric process, $H_f - H_i = Q = \int_i^f C_P dT$
# Adiabatic process $U_f - U_i = - \int_i^f PdV$	# Adiabatic process, $H_f - H_i = \int_i^f VdP$
# Free expansion, $U_i = U_f$	# Throttling process, $H_i = H_f$
# For an ideal gas $U = \int C_V dT + \text{constant}$	# For an ideal gas, $H = \int C_P dT + \text{constant}$
# Nearby equilibrium states $dU = Tds - PdV$, $T = \left(\frac{\partial U}{\partial S}\right)_V$ $P = -\left(\frac{\partial U}{\partial V}\right)_S$	# Nearby equilibrium states $dH = Tds + VdP$, $T = \left(\frac{\partial H}{\partial S}\right)_P$, $V = \left(\frac{\partial H}{\partial P}\right)_S$

Joule - Thomson/Kelvin effect : Adiabatic Throttling of gases

Gay-Lussac & Joule's experiments independently showed that $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for perfect gases but with real gases slight cooling was found, meaning $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$. To find out the relation, Lord Kelvin modified the Gay-Lussac-Joule's experiments, known as "Porous plug experiment". A highly compressed gas is continuously forced at constant pressure through a constricted nozzle to throttle & thus to expand in volume. We already learned that $H_i = H_f$. Now we calculate the change in temperature.

$$\begin{aligned} \text{Given } H = U + PV \Rightarrow dH &= dU + PdV + VdP = \delta Q + VdP = Tds + VdP \\ \therefore 0 &= T \left[\left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT \right] + VdP \\ \therefore 0 &= -T \left(\frac{\partial V}{\partial T} \right)_P dP + \left(\frac{\partial S}{\partial T} \right)_P dT + VdP \quad \left[\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \right] \end{aligned}$$

$$\therefore C_p dT - \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] dp = 0$$

$$\therefore \left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] = \mu, \text{ or } AT = \int_{P_1}^{P_2} \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] dp$$

$$\mu = \frac{T^2}{C_p} \frac{\partial}{\partial T} \left(\frac{V}{T} \right)$$

$$\text{for perfect gas, } T \left(\frac{\partial V}{\partial T} \right)_p - V = T \frac{V}{T} - V = 0$$

Hence the J-T effect vanishes for ideal gas.

$$\text{Again, } C_p dT = - \left[T \left(\frac{\partial S}{\partial P} \right)_T + V \right] dp$$

$$\therefore C_p \left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\partial U}{\partial P} \right)_T - \frac{\partial}{\partial P} (PV) \quad \text{as } T dS = dU + PdV$$

J-T effect

Deviation from Joule's law

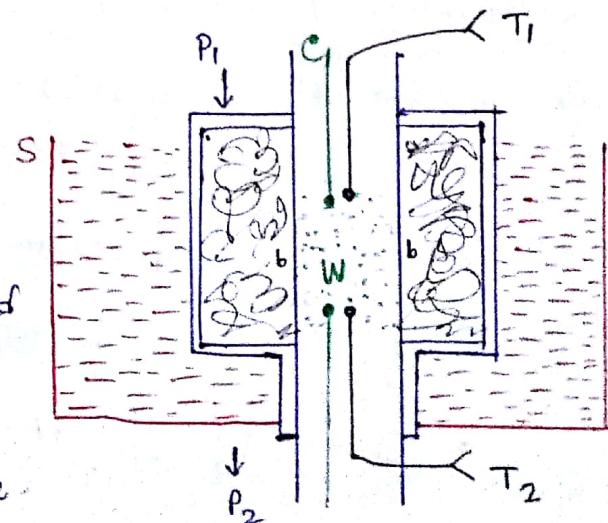
Deviation from Boyle's law

Now $\left(\frac{\partial U}{\partial P} \right)_T < 0$ because internal energy decreases with decreasing volume (or increase of pressure). \therefore Due to deviation from Joule's law, J.T. effect will be a cooling effect ($\left(\frac{\partial T}{\partial P} \right)_H > 0$) mean fall of temperature per unit fall in pressure. The effect of deviations from Boyle's law can be a cooling ($\left(\frac{\partial PV}{\partial P} \right) < 0$) or heating ($\left(\frac{\partial PV}{\partial V} \right) > 0$) effect.

\uparrow
[H₂, He]

The porous plug Experiment

Joule & Thomson employed a cylindrical plug where the compressed gas flows through a copper tube immersed in a thermostat to the porous plug, which consists of silk, cotton wool or other porous materials W between two piece of wire gauge I enclosed in a cylinder of (nonconducting) wood



bb. The plug and part of the tube is surrounded by asbestos contained in a tin cylinder so that no heat reaches from the bath. The temperature drop is measured by the thermocouples. They worked with O_2 , N_2 , CO_2 within $4^\circ C$ & $100^\circ C$ with initial pressure 4.5 atm & final pressure 1 atm.

A small cooling effect on expansion is seen for gases while for H_2 , He (surprisingly) heating on expansion is seen. This paradox was resolved by applying van der Waal's equation of state.

We have $\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right]$. Using VN equation of state

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

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

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

$$\therefore \mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left[\frac{RT}{V-b} \left\{ \frac{1}{-\frac{2a}{V^3} + \frac{RT}{(V-b)^2}} \right\} - V \right]$$

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

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

$\therefore \mu > 0$ if $\frac{2a}{RT} > b$, $\therefore T < \frac{2a}{Rb}$ and this gives cooling effect.

At $T > \frac{2a}{Rb}$, the gas is heated on suffering J-T expansion. The

temperature $T = \frac{2a}{Rb}$ is called the temperature of inversion. One can

show that $T_i = \frac{2a}{Rb} = \frac{27}{4} T_c$ with T_c = critical temperature of the gas and this relation is approximately true because van der Waal's equation isn't accurate for real gases.

For N_2 , O_2 , CO_2 etc, T_i is greater than the temperature at which J-T expansion was carried out, hence a cooling effect was obtained.

for H_2 , He, $T_i < 300K$, no heating effect was found. It was found later that if H_2 , He are sufficiently precooled then they exhibit cooling on J-T expansion.

If we don't neglect $\frac{b}{V}$ and $\frac{2a}{RTV}$ term in μ , then for very

high pressures,

$$\mu \approx \frac{1}{C_p} \left[\frac{2a}{RT} - b - \frac{6ab}{R^2 T^2} p \right]$$

and for van der Waals gas, $C_p = C_{p_0} + \frac{2a}{RT^2} - \frac{3ab}{R^2 T^3} p^2$

Combination of above gives

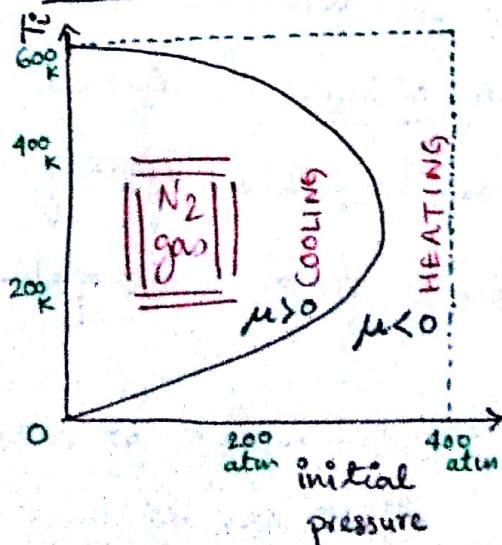
$\mu = \mu(p, T)$. The experimental results of J-T effect on N_2 is shown for different initial pressures.

Observations

(a) For equal temperature, μ is greater at lower initial pressures in accordance with

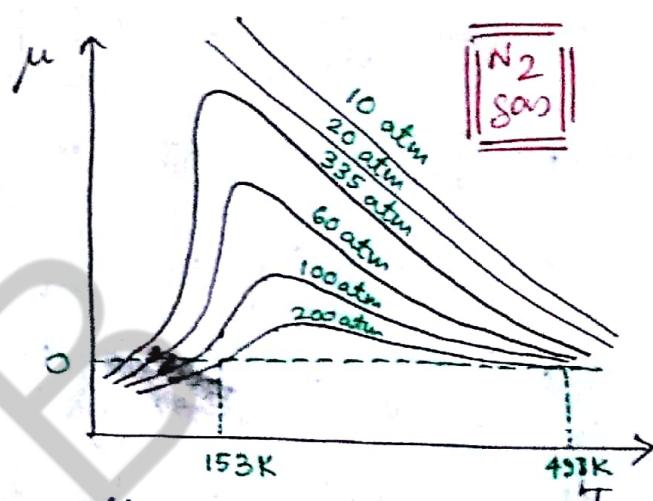
$\mu = \frac{1}{C_p} \left(\frac{2a}{RT} - b - \frac{6ab}{R^2 T^2} p \right)$, (b) for a definite pressure, μ passes through a maximum & decreases to zero on both sides. So there exist two inversion temperatures for J-T effect corresponding to an initial pressure. For example at 200 atm for N_2 $\mu=0$ happens at $-120^\circ C = 153K$ & other at $225^\circ C = 498K$.

Curve of inversion



Temperature of inversion depends on the initial pressure. Inversion curve gives inversion temperature at different initial pressure. Roebuck & Osterberg obtained the experimental graph shown beside.

To have a cooling effect, the J-T expansion should be carried out at points to the left of the inversion curve. This can be explained by considering the reduced equation of state of van der Waals gas.



In term of P^* , V^* , T^* , $\mu = \frac{1}{C_P} \left[T^* \left(\frac{\partial V^*}{\partial T^*} \right)_{P^*} - V^* \right]$ and

$$\frac{8}{3} T^* = \left(P^* + \frac{3}{V^{*2}} \right) (V^* - \frac{1}{3}), \text{ differentiating,}$$

$$\frac{8}{3} \left(\frac{\partial T^*}{\partial V^*} \right)_{P^*} = P^* + \frac{3}{V^{*2}} - \frac{6}{V^{*3}} (V^* - \frac{1}{3})$$

$$\begin{aligned} \therefore \mu &= \frac{1}{C_P} \left[\frac{T^*}{\frac{3}{8} \left(P^* + \frac{3}{V^{*2}} - \frac{6}{V^{*3}} + \frac{2}{V^{*3}} \right)} - V^* \right] = \frac{1}{C_P} \frac{\left[\frac{8}{3} T^* - V^* \left(P^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}} \right) \right]}{\left(P^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}} \right)} \\ &= \frac{\left(P^* + \frac{3}{V^{*2}} \right) (V^* - \frac{1}{3}) - V^* \left(P^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}} \right)}{C_P \left(P^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}} \right)} = \frac{\left(-\frac{P^*}{3} + \frac{6}{V^*} - \frac{3}{V^{*2}} \right)}{C_P \left(P^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}} \right)} \\ &= \frac{\left(-\frac{P^*}{3} + \frac{6}{V^*} - \frac{3}{V^{*2}} \right)}{\left[\frac{8}{3} C_P \left(\frac{\partial T^*}{\partial V^*} \right)_{P^*} \right]} \end{aligned}$$

. Here the denominator is always positive because $\left(\frac{\partial T^*}{\partial V^*} \right)_{P^*} > 0$.

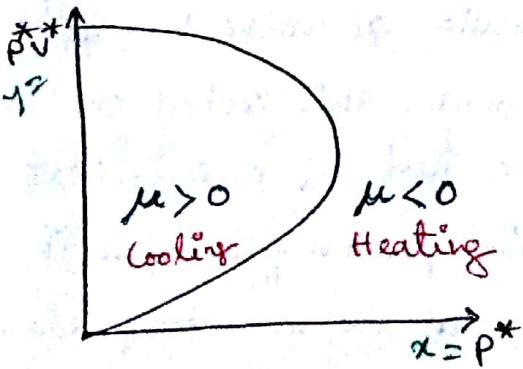
$$\therefore \begin{cases} \mu > 0 & \text{if } \frac{P^*}{3} < \frac{6}{V^*} - \frac{3}{V^{*2}} \Rightarrow P^* < \frac{9(2V^*-1)}{V^{*2}} & \xrightarrow{\text{Cooling}} \\ \mu < 0 & \text{if } P^* > \frac{9(2V^*-1)}{V^{*2}} & \xrightarrow{\text{Heating}} \end{cases}$$

Thus inversion occurs at $P^* = \frac{9(2V^*-1)}{V^{*2}}$ and in that state the gas cannot undergo a change in temperature.

$$\text{Setting } P^* = x, P^* V^* = y \text{ we have } P^* V^{*2} = 9(2P^* V^* - P^*)$$

$$\Rightarrow y^2 = 9(2y - x) \text{ representing}$$

a parabola. Here $\mu > 0$ means $9x < 18y - y^2$ which are points inside the curve with cooling effect & for points outside, $\mu < 0$ and heating effect takes place. The temperature of inversion is obtained by putting P^* in reduced VW state

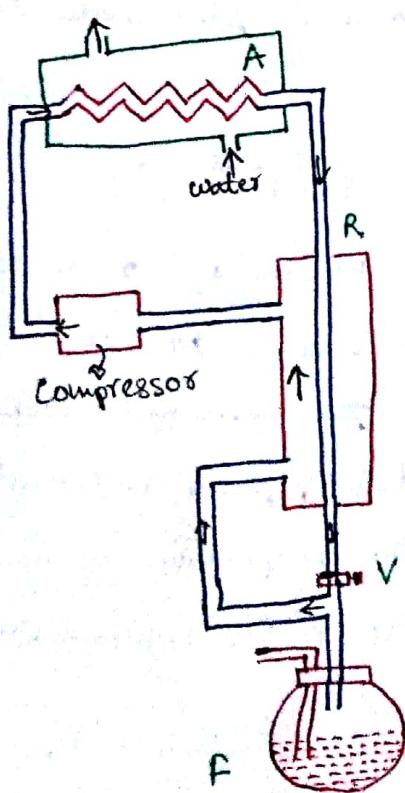


$$T_i = \frac{3}{4} \left(3 - \frac{1}{V^*} \right)^2$$

Principle of Regenerative cooling

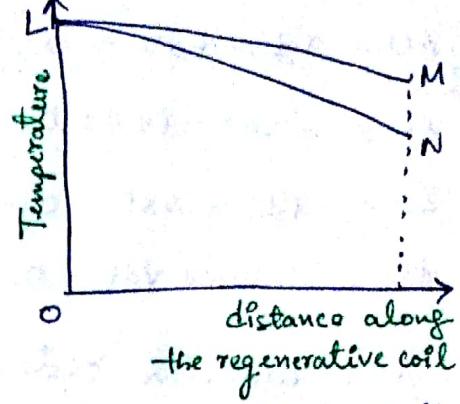
Joule-Thomson cooling that depends on the pressure difference on the sides of the porous plug is observed to be very small for most of the gases. For air at 20°C temperature with pressure on two sides at 50 atm & 1 atm, Joule-Thomson found that the temperature falls by 11.7°C only. Even using a pressure of 210 atm instead of 50 atm, the cooling was only 42°C . However the cooling effect can be intensified by employing regenerative cooling.

A portion of the gas which first suffers J-T expansion and becomes cooled is employed to cool other portions of the incoming gas before it later reaches the nozzle. The incoming gas becomes more cooled after traversing the nozzle. In this way the cooling effect can be cumulatively rendered. In this method the extra advantage is the lower the temperature, the greater is the J-T cooling.



The high pressure gas from compressor enters the spirals contained in the water cooled jacket A where the heat of compression is removed. The gas enters the regenerator R and suffers J-T expansion at valve V & gets cooled by small amount. This cooled gas returns by the outer tube & absorbs heat from the incoming high pressure gas before it reaches the compressor at the same temperature as the incoming gas at R. The gas is again compressed, cooled by A and reenters at R. In a time interval, the gas approaching V becomes cooled more & more till the J-T cooling at V is sufficiently to liquefy the gas. A portion of the escaping gas then condenses inside

the Dewar flask F. At this stage the temperature throughout the apparatus become steady. LM represents the continual decrease of temperature of the gas as we approach the nozzle V through the inner tube, while MN represents the J-T cooling. NL represents the temperature of the low-pressure gas which is less than that of the adjacent high pressure gas at each point of the coil. Thus, the low pressure gas extracts heat from the incoming gas.



Thermodynamic Potentials : Helmholtz & Gibbs free energy

There are 4 thermodynamic potentials

- ① Internal Energy : U
- ② Helmholtz free Energy : F
- ③ Enthalpy : H
- ④ Gibbs function : G

We know internal energy is the total energy of the system. Using 1st & 2nd law we know

$$dU = TdS - PdV. \quad \text{--- } ①$$

The function $F = U - TS$ is known as Helmholtz free energy function. While TS is the energy associated with disorder & unavailable so $U - TS$ energy can be extracted from the system to do work. Hence the term "free".

Any small change is $dF = dU - TdS - SdT$
and we know $dU = TdS + PdV$. $\therefore dF = TdS - PdV - TdS - SdT$
or $dF = -PdV - SdT$ --- ②

Similarly total heat content is $H = U + PV$

$$\therefore dH = dU + PdV + VdP = TdS - PdV + PdV + VdP$$

$$\underline{dH = TdS + VdP} \quad \text{--- } ③$$

Similarly Gibbs function is $G = U - TS + PV = H - TS$

$$\therefore dG = dH - TdS - SdT = TdS + VdP - TdS - SdT$$

$$\underline{dG = VdP - SdT} \quad \text{--- } ④$$

$dU = TdS - PdV = 0$, isochoric adiabatic process, $U = \text{constant}$

$dF = -SdT - PdV = 0$, isochoric isothermal process, $F = \text{constant}$

$dH = TdS + VdP = 0$, isobaric adiabatic process, $H = \text{constant}$

$dG = -SdT + VdP = 0$, isobaric isothermal process, $G = \text{constant}$

A mechanical system is in stable equilibrium when potential energy is minimum. In thermodynamics, U, F, H, G plays the role of P.E. The direction of isothermal-isochoric process is to make F minimum. In isothermal-isobaric process G tends to be minimum & for isobaric-adiabatic process, H tends to be minimum.

Relation of T.D. potentials with their variables

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

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

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

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

Similarly dH is a perfect differential,

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

So as dG a perfect differential, $\left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right)_P\right]_T$

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

Four Maxwell's T.D. relation.

Relation amongst T.D. potentials, $U = F + TS = F - T \left(\frac{\partial F}{\partial T}\right)_V$

$$H = G + TS = G - T \left(\frac{\partial G}{\partial T}\right)_P$$

Chemical potential and Gibbs-Duhem equation

Just like U and S , thermodynamic quantities F, H, G have the additivity property, if P & T remains constant. This means that when the amount of matter (N number of particles) is changed by a given factor, T.D. changes similarly or the T.D. quantity is a homogeneous function of first order with respect to the additive variable.

$$\therefore U = N U \left(\frac{S}{N}, \frac{V}{N} \right), \quad F = N F \left(\frac{V}{N}, T \right), \quad H = N H \left(\frac{S}{N}, P \right)$$

$G = N G (P, T)$. So we have essentially regarded N as a parameter then for a change dN , we can write

where the "chemical potential" is defined to be

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \left(\frac{\partial H}{\partial N} \right)_{T,V} = \left(\frac{\partial G}{\partial N} \right)_{P,T}$$

and the general equation

$$U(S, \{x_i\}, \{N_j\}) = TS + \sum_i x_i x_i + \sum_j \mu_j N_j$$

is called "Gibbs-Duhem equation"

$\underbrace{x_i}_{\text{Generalized force}} - \underbrace{\sum_j \mu_j N_j}_{\text{Generalized displacement}}$

This is a very important equation in Chemical Thermodynamics.

for any single valued function $\phi(x_1, x_2, \dots, x_n)$ $\frac{\partial}{\partial x_i} \left(\frac{\partial \phi}{\partial x_j} \right) = \frac{\partial}{\partial x_j} \left(\frac{\partial \phi}{\partial x_i} \right)$
we recover Maxwell relations with additional Maxwell relations

$$\left(\frac{\partial S}{\partial N} \right)_{V,T} = - \left(\frac{\partial \mu}{\partial T} \right)_{V,N}, \quad \left(\frac{\partial P}{\partial N} \right)_{V,T} = - \left(\frac{\partial \mu}{\partial V} \right)_{T,N} \quad \text{from Helmholtz free energy}$$

$$\text{Similarly } \left(\frac{\partial V}{\partial N} \right)_{P,T} = \left(\frac{\partial \mu}{\partial P} \right)_{T,N}, \quad \left(\frac{\partial S}{\partial N} \right)_{P,T} = - \left(\frac{\partial \mu}{\partial T} \right)_{P,N} \quad \text{from Gibbs free energy}$$

Gibbs-Duhem equation for a single component PVT system reduces to

$$U = TS - PV + \mu N \quad \Leftrightarrow \quad G = \mu N$$

We will use this results to discuss the phase equilibria & phase transitions.