Module 4

Thermodynamic Relations

- *properties are point functions* → *exact differentials*
- *the state of a <u>simple compressible system</u> is completely specified by any* *two independent intensive properties.*
- Measurable properties (p, T, v, etc.)
- Immeasurable properties (h, u, s etc.)

- *Some Mathematical theorems*

- *A property of a single component system may be written as a general mathematical function $z = z(x,y)$)………ex: $P = P(T, v)$*

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

$$dz = M\,dx + N\,dy$$

For exact differentials,

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \ldots\ldots Cross\ Derivative\ theorem$$

If, x= x(y,z) and Y = y(z,x)

$$\left[\frac{\partial x}{\partial y}\right]_z = \frac{1}{\left[\frac{\partial y}{\partial x}\right]_z} \quad \ldots\ldots.Reciprocity\ relation$$

$$\left[\frac{\partial x}{\partial y}\right]_z \left[\frac{\partial y}{\partial z}\right]_x \left[\frac{\partial z}{\partial x}\right]_y = -1 \quad \ldots\ldots\ldots.Cyclic\ relation$$

- _Combined first and second law equations_

$$du = Tds - pdv$$

$$dh = Tds + vdp$$

Helmholtz and Gibbs functions.

- *Free Energy → "useful" work*

Helmholtz Free Energy, F, (@ T=c, v=c)

F = U – TS   or   f = u - Ts

ΔF= useful work from a system

Gibbs Free Energy, G, (@ T=c, p=c)

G = H – TS   or   g = h – Ts

ΔG= useful work from a chemical reaction

$$df = -pdv - sdT$$

$$dg = vdp - sdT$$

Thermodynamic potentials

- $du = Tds - pdv \ldots\ldots C_1$
- $dh = Tds + vdp \ldots\ldots C_2$
- $dg = vdp - sdT \ldots\ldots C_3$
- $df = -pdv - sdT \ldots\ldots C_4$

$Clausius$
$equations$

Maxwell relations

All the four energy relations $C_1, C_2, C_3 \, and \, C_4$ are functions of state variables (properties) and hence, the exactness criteria of differential equation can be applied.

- $C_1 \Rightarrow u = Tds - pdv$

    $i.e. \quad du = Mds + Ndv \qquad where, \qquad M \equiv T \ and \ N \equiv -p$

For differential of function 'u' to be exact:

$$\left[\frac{\partial M}{\partial v}\right]_s = \left[\frac{\partial N}{\partial s}\right]_v \ldots\ldots Cross \ derivative \ theorem$$

$$\boxed{\left[\frac{\partial T}{\partial v}\right]_s = -\left[\frac{\partial p}{\partial s}\right]_v \ldots\ldots M_1}$$

- $C_2 \Rightarrow dh = Tds + vdp$

$$\boxed{\left[\frac{\partial T}{\partial p}\right]_s = \left[\frac{\partial v}{\partial s}\right]_p \quad \ldots\ldots. M_2}$$

- $C_3 \Rightarrow dg = vdp - sdT$

$$\boxed{\left[\frac{\partial v}{\partial T}\right]_p = -\left[\frac{\partial s}{\partial p}\right]_T \quad \ldots\ldots. M_3}$$

- $C_4 \Rightarrow df = -pdv - sdT$

$$\boxed{\left[\frac{\partial p}{\partial T}\right]_v = \left[\frac{\partial s}{\partial v}\right]_T \quad \ldots\ldots. M_4}$$

The mnemonic diagram can help to obtain the Maxwell relations.
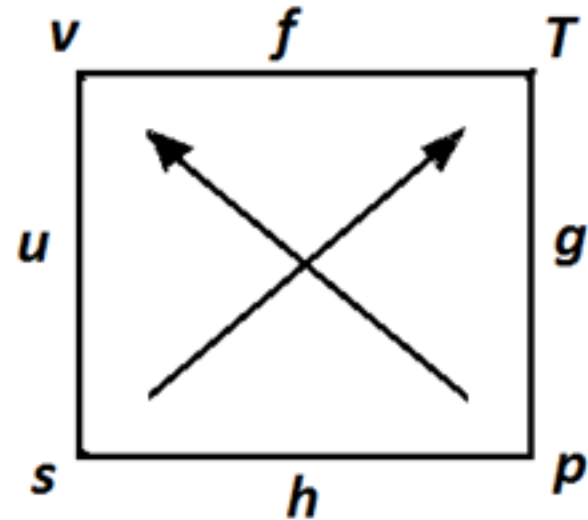
Using 'corner relations' from the square.

$$\left[\frac{\partial T}{\partial v}\right]_s = -\left[\frac{\partial p}{\partial s}\right]_v \quad \ldots\ldots M_1$$

$$\left[\frac{\partial T}{\partial p}\right]_s = \left[\frac{\partial v}{\partial s}\right]_p \quad \ldots\ldots\ldots M_2$$

$$\left[\frac{\partial v}{\partial T}\right]_p = -\left[\frac{\partial s}{\partial p}\right]_T \quad \ldots\ldots M_3$$

$$\left[\frac{\partial p}{\partial T}\right]_v = \left[\frac{\partial s}{\partial v}\right]_T \quad \ldots\ldots\ldots M_4$$
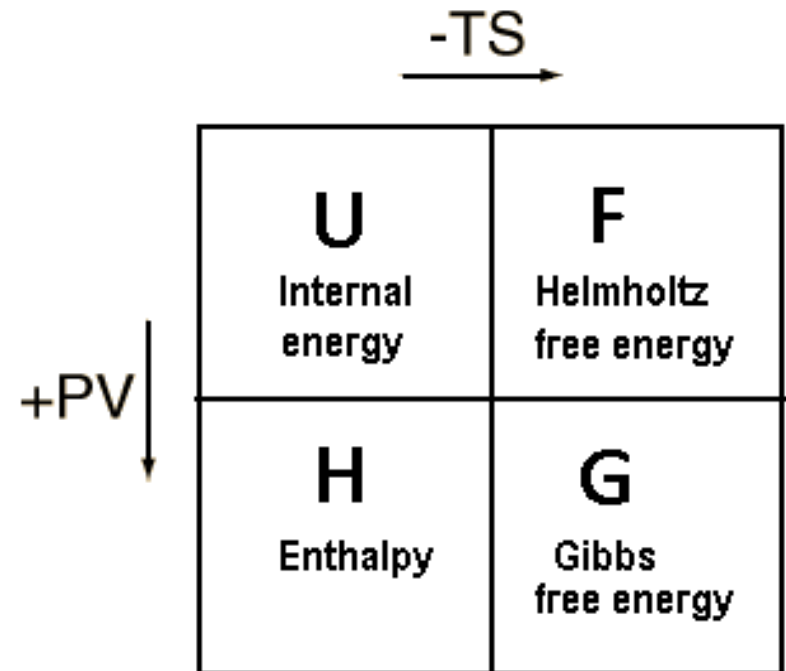
This mnemonic diagram can help to track the relationships between the four thermodynamic potentials U, H, F and G
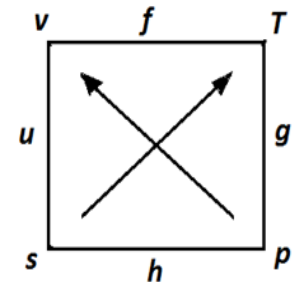
F = U − TS

G = H − TS

H = U + PV

- $C_1 \Rightarrow du = Tds - pdv$ ……………(1)
- $u = u(s, v)$

$$\therefore du = \left[\frac{\partial u}{\partial s}\right]_v ds + \left[\frac{\partial u}{\partial v}\right]_s dv \ \text{………}(2)$$

Comparing (1) and (2),

$$\boxed{\left[\frac{\partial u}{\partial s}\right]_v = T \quad and \quad \left[\frac{\partial u}{\partial v}\right]_s = -p}$$
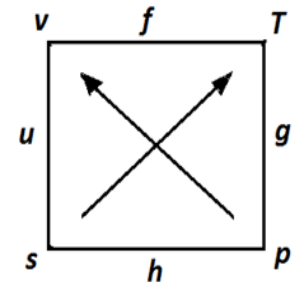
- $C_2 \Rightarrow dh = Tds + vdp \ldots\ldots\ldots\ldots\ldots. (3)$
- $h = h\,(s, p)$

$$\therefore dh = \left[\frac{\partial h}{\partial s}\right]_p ds + \left[\frac{\partial h}{\partial p}\right]_s dp \ \ldots\ldots\ldots..\ldots (4)$$

Comparing (3) and (4),

$$\boxed{\left[\frac{\partial h}{\partial s}\right]_p = T \quad and \quad \left[\frac{\partial h}{\partial p}\right]_s = v}$$
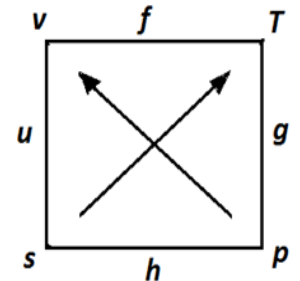
- $C_3 \Rightarrow dg = vdp - sdT \ldots \ldots \ldots (5)$
- $g = g(p, T)$

$$\therefore dg = \left[\frac{\partial g}{\partial p}\right]_T dp + \left[\frac{\partial g}{\partial T}\right]_p dT \ldots \ldots (6)$$

Comparing (5) and (6),

$$\boxed{\left[\frac{\partial g}{\partial p}\right]_T = v \quad and \quad \left[\frac{\partial g}{\partial T}\right]_p = -s}$$
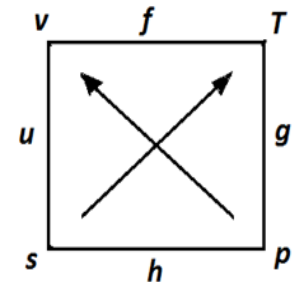
- $C_4 \Rightarrow df = -pdv - sdT \ldots\ldots\ldots(7)$
- $f = f(v, T)$

$$\therefore df = \left[\frac{\partial f}{\partial v}\right]_T dv + \left[\frac{\partial f}{\partial T}\right]_v dT \ldots(8)$$

Comparing (7) and (8),

$$\boxed{\left[\frac{\partial f}{\partial v}\right]_T = -p \quad and \quad \left[\frac{\partial f}{\partial T}\right]_v = -s}$$

Description	Definition
Specific heat at constant volume	$C_v = \left[\dfrac{\partial u}{\partial T}\right]_v$
Specific heat at constant pressure	$C_p = \left[\dfrac{\partial h}{\partial T}\right]_p$
Coefficient of volume expansion	$\beta = \dfrac{1}{v}\left[\dfrac{\partial v}{\partial T}\right]_p$
Isothermal compressibility factor	$K_T = -\dfrac{1}{v}\left[\dfrac{\partial v}{\partial p}\right]_T$
Isentropic compressibility factor	$K_s = \propto = -\dfrac{1}{v}\left[\dfrac{\partial v}{\partial p}\right]_s$
Joule Thomson coefficient	$\mu_{JT} = \left[\dfrac{\partial T}{\partial p}\right]_h$

Tds Equations

$$(1^{st} \, Tds \, equation). \quad Tds = C_v dT + T \left[\frac{\partial p}{\partial T}\right]_v dv$$
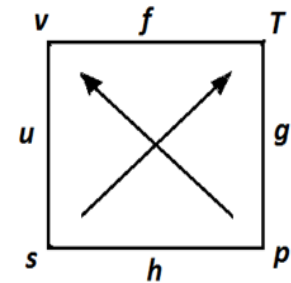
$$(2^{nd} \, Tds \, equation). \quad Tds = C_p dT - T \left[\frac{\partial v}{\partial T}\right]_p dp$$

- $s = s(v, T)$

$$ds = \left[\frac{\partial s}{\partial v}\right]_T dv + \left[\frac{\partial s}{\partial T}\right]_v dT$$

- $\left[\frac{\partial s}{\partial v}\right]_T = \left[\frac{\partial p}{\partial T}\right]_v \ldots\ldots Maxwell\ relation.$

- Also, $\left[\frac{\partial s}{\partial T}\right]_v = \left[\left(\frac{\partial s}{\partial u}\right)\cdot\left(\frac{\partial u}{\partial T}\right)\right]_v = \frac{1}{T} C_v$

$$ds = \frac{C_v}{T} dT + \left[\frac{\partial p}{\partial T}\right]_v dv$$

$$\therefore Tds = C_v dT + T\left[\frac{\partial p}{\partial T}\right]_v dv$$

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

- $\left[\dfrac{\partial p}{\partial T}\right]_v = \dfrac{\beta}{K}$ ... ... From cyclic relation

$$\therefore Tds = \ C_v dT + \frac{\beta}{K} T dv$$

- $ds = \dfrac{C_v}{T} dT + \left[\dfrac{\partial p}{\partial T}\right]_v dv$
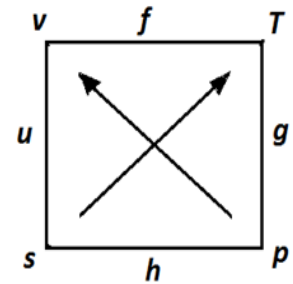
- $ds = MdT + Ndv$

$$hence, \left[\frac{\partial\, C_v}{\partial v}\right]_T = T \left[\frac{\partial^2 p}{\partial T^2}\right]_v$$

- $s = s(T, p)$

$$ds = \left[\frac{\partial s}{\partial T}\right]_p dT + \left[\frac{\partial s}{\partial p}\right]_T dp$$

- $\left[\frac{\partial s}{\partial p}\right]_T = -\left[\frac{\partial v}{\partial T}\right]_p .. Maxwell\ relation$

- Also, $\left[\frac{\partial s}{\partial T}\right]_p = \left[\left(\frac{\partial s}{\partial h}\right) \cdot \left(\frac{\partial h}{\partial T}\right)\right]_p = \frac{1}{T} C_p$

$$\boxed{Tds = C_p dT - T\left[\frac{\partial v}{\partial T}\right]_p dp}$$

- $\beta = \frac{1}{v}\left[\frac{\partial v}{\partial T}\right]_p$

$$\boxed{Tds = C_p dT - \beta T v dp}$$

- $ds = \frac{C_p}{T} dT - \left[\frac{\partial v}{\partial T}\right]_p dp$
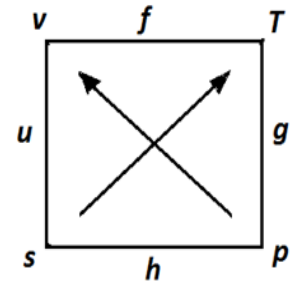
- $ds = M dT + N dp$

$$\boxed{hence, \left[\frac{\partial C_p}{\partial p}\right] = -T \left[\frac{\partial^2 v}{\partial T^2}\right]_p}$$

- $s = s(p, v)$

$$ds = \left[\frac{\partial s}{\partial p}\right]_v dp + \left[\frac{\partial s}{\partial v}\right]_p dv$$

- $\left[\dfrac{\partial s}{\partial p}\right]_v dp = \left[\dfrac{\partial s}{\partial u} \quad \dfrac{\partial u}{\partial T} \quad \dfrac{\partial T}{\partial p}\right]_v dp = \dfrac{1}{T} \; C_v \left(\dfrac{\partial T}{\partial p}\right)_v dp$

- $\left[\dfrac{\partial s}{\partial v}\right]_p dv = \left[\dfrac{\partial s}{\partial h} \quad \dfrac{\partial h}{\partial T} \quad \dfrac{\partial T}{\partial v}\right]_p dv = \dfrac{1}{T} \; C_p \left(\dfrac{\partial T}{\partial v}\right)_p dv$

$$ds = \frac{1}{T} \; C_v \left(\frac{\partial T}{\partial p}\right)_v dp + \frac{1}{T} \; C_p \left(\frac{\partial T}{\partial v}\right)_p dv$$

$$\boxed{hence, \qquad Tds = C_v \left[\frac{\partial T}{\partial p}\right]_v dp + C_p \left[\frac{\partial T}{\partial v}\right]_p dv}$$

- $Tds = C_v \left[\dfrac{\partial T}{\partial p}\right]_v dp + C_p \left[\dfrac{\partial T}{\partial v}\right]_p dv$

- $\dfrac{\beta}{K} = \dfrac{\frac{1}{v}\left[\frac{\partial v}{\partial T}\right]_p}{-\frac{1}{v}\left[\frac{\partial v}{\partial p}\right]_T} = -\left[\dfrac{\partial v}{\partial T}\right]_p \cdot \left[\dfrac{\partial p}{\partial v}\right]_T \;\Rightarrow\; \left[\dfrac{\partial p}{\partial T}\right]_v = \dfrac{\beta}{K}$

- $\left[\dfrac{\partial T}{\partial v}\right]_p = \dfrac{1}{v\beta}$

$$\boxed{Tds = \dfrac{K\,C_v}{\beta}\,dp + \dfrac{C_p}{\beta v}\,dv}$$

Energy equation

Internal energy

- $du = Tds - pdv$

- $Tds = C_v dT + T\left[\dfrac{\partial p}{\partial T}\right]_v dv$

$\rightarrow$ $\therefore\ du = C_v\,dT + \left[T\left(\dfrac{\partial p}{\partial T}\right)_v - p\right]dv$

- *For an ideal gas,* $pv = RT$

$$\therefore \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v} = \frac{p}{T}$$

- *hence,* $\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] = 0$

$$\Rightarrow \ du = \ C_v \, dT$$

Thus, $\qquad u = u(T)$ *only*

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

$$Thus, \, du = \, C_v \, dT + \left[\frac{\beta T}{K} - p\right] dv$$

Energy equation

Enthalpy

- $dh = Tds + vdp$

- $Tds = C_p dT - T \left[\dfrac{\partial v}{\partial T} \right]_p dp$

➔ $$dh = C_p\, dT - \left[T \left(\dfrac{\partial v}{\partial T} \right)_p - v \right] dp$$

- *For an ideal gas,* $pv = RT$

$$\therefore \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} = \frac{v}{T}$$

- *hence,* $\left[T \left(\frac{\partial v}{\partial T}\right)_p - v \right] = 0$

$\Rightarrow dh = C_p \, dT$

Thus, $h = h(T)$ *only*

Difference in Heat Capacities

- *Combining the Tds equations,*

$$Tds = C_p dT - T \left[\frac{\partial v}{\partial T} \right]_p dp = C_v dT \ + \ T \left[\frac{\partial p}{\partial T} \right]_v dv$$

$$dT = \left[\frac{T}{C_p - C_v} \right] \left[\left[\frac{\partial v}{\partial T} \right]_p dp + \left[\frac{\partial p}{\partial T} \right]_v dv \right]$$

- $dT = \left[\left[\dfrac{T}{C_p - C_v} \right] \left[\dfrac{\partial v}{\partial T} \right]_p dp + \left[\dfrac{T}{C_p - C_v} \right] \left[\dfrac{\partial p}{\partial T} \right]_v dv \right]$

- $Considering, \quad T = T(p, v)$

- $dT = \left[\dfrac{\partial T}{\partial p} \right]_v dp + \left[\dfrac{\partial T}{\partial v} \right]_p dv$

- $\left[\dfrac{\partial T}{\partial p} \right]_v = \left[\dfrac{T}{C_p - C_v} \right] \left[\dfrac{\partial v}{\partial T} \right]_p$

$$(C_p - C_v) = T \left[\dfrac{\partial v}{\partial T} \right]_p \left[\dfrac{\partial p}{\partial T} \right]_v$$

For an ideal gas, $\qquad pv = RT$

$$\therefore \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} \ and \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$$

- $(C_p - C_v) = T \left[\frac{R}{p}\right] \left[\frac{R}{v}\right] = \frac{TRR}{pv} = \frac{TRR}{RT} = R$

$$\boxed{\textcolor{red}{C_p - C_v = R}}$$

$$(C_p - C_v) = T \left[\frac{\partial v}{\partial T}\right]_p \left[\frac{\partial p}{\partial T}\right]_v$$

Also,

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

$\therefore \left[\frac{\partial p}{\partial T}\right]_v = - \left[\frac{\partial p}{\partial v}\right]_T \left[\frac{\partial v}{\partial T}\right]_p$

$$i.e. \ C_p - C_v = -T \left[\left(\frac{\partial v}{\partial T}\right)_p\right]^2 \left[\frac{\partial p}{\partial v}\right]_T$$

- $$C_p - C_v = -T \left[\left(\frac{\partial v}{\partial T} \right)_p \right]^2 \left[\frac{\partial p}{\partial v} \right]_T$$

- $$\frac{\beta^2}{K} = \frac{\left[\frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \right]^2}{-\frac{1}{v} \left[\frac{\partial v}{\partial p} \right]_T} = -\frac{1}{v} \left[\left(\frac{\partial v}{\partial T} \right)_p \right]^2 \cdot \left[\frac{\partial p}{\partial v} \right]_T$$

$$\boxed{C_p - C_v = \frac{vT\beta^2}{K}}$$

$$Since, v, T, \beta^2 \text{ and } K \text{ are positive quanties}, C_p > C_v$$

Ratio of specific heats

$$Tds = C_v \left[\frac{\partial T}{\partial p}\right]_v dp + C_p \left[\frac{\partial T}{\partial v}\right]_p dv$$

- *For an isentropic process,* $ds = 0$

$$\Rightarrow\ 0 = C_v \left[\frac{\partial T}{\partial p}\right]_v dp + C_p \left[\frac{\partial T}{\partial v}\right]_p dv$$

$$i.e.\ \ C_p\left[\frac{\partial T}{\partial v}\right]_p dv = -C_v \left[\frac{\partial T}{\partial p}\right]_v dp$$

$$\frac{C_p}{C_v} = -\frac{\left[\frac{\partial T}{\partial p}\right]_v dp}{\left[\frac{\partial T}{\partial v}\right]_p dv} = -\frac{\left[\frac{\partial T}{\partial p}\right]_v \left[\frac{dp}{dv}\right]_s}{\left[\frac{\partial T}{\partial v}\right]_p} = -\left[\frac{\partial T}{\partial p}\right]_v \left[\frac{dp}{dv}\right]_s \left[\frac{\partial v}{\partial T}\right]_p$$

- $\left[\frac{\partial p}{\partial v}\right]_T \left[\frac{\partial v}{\partial T}\right]_p \left[\frac{\partial T}{\partial p}\right]_v = -1 \ \ldots\ldots\ Cyclic\ relation$

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

- $\frac{C_p}{C_v} = -\left[\frac{\partial T}{\partial p}\right]_v \left[\frac{dp}{dv}\right]_s \left[\frac{\partial v}{\partial T}\right]_p = \frac{\left[\frac{dp}{dv}\right]_s}{\left[\frac{\partial p}{\partial v}\right]_T} = \frac{K_T}{K_S} = \gamma$

- $= \dfrac{Slope\ of\ isentropic\ curve\ on\ the\ p-v\ plane}{Slope\ of\ isothermal\ curve\ on\ the\ same\ p-v\ plane}$
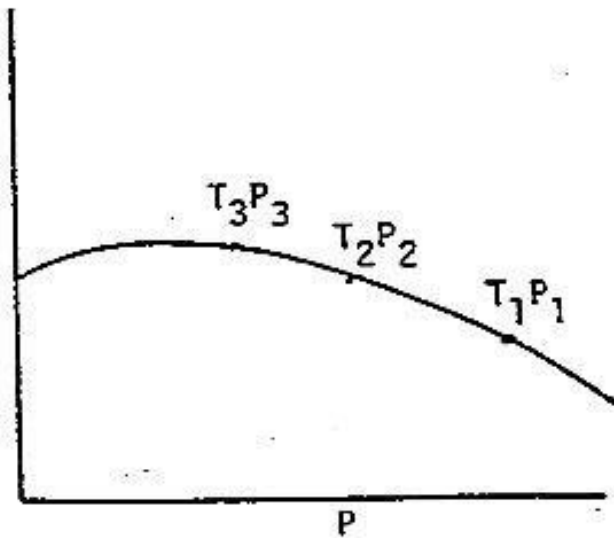
Joule Thomson effect
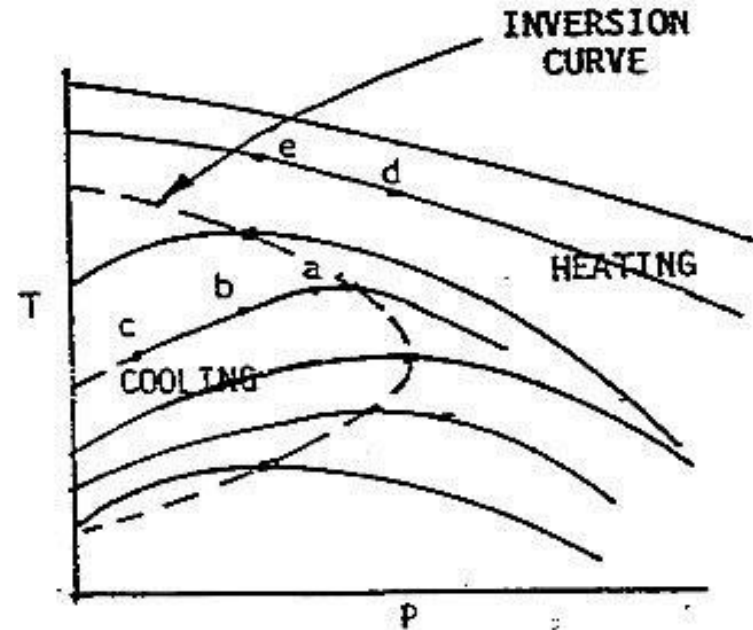

Fig. 3a Points of equal enthalpy

Fig. 3b Isenthalpic curves and the enthalpy. inversion curve.

- *Joule-Thomson coefficient,* $\mu_{JT} = \left[\dfrac{\partial T}{\partial p}\right]_h$

- $0 = C_p \, dT - \left[T \left(\dfrac{\partial v}{\partial T}\right)_p - v\right] dp$

$$\mu_{JT} = \left[\dfrac{\partial T}{\partial p}\right]_h = \dfrac{1}{C_p}\left[T\left(\dfrac{\partial v}{\partial T}\right)_p - v\right]$$

- *For an ideal gas* ⇨ $pv = RT$

- $\left(\dfrac{\partial v}{\partial T}\right)_p = \dfrac{R}{p} = \dfrac{v}{T}$

- $\mu_{JT} = \left[\dfrac{\partial T}{\partial p}\right]_h = \dfrac{1}{C_p}\left[T\,\dfrac{v}{T} - v\right] = 0$

$$\boxed{\textit{For an ideal gas,} \qquad \mu_{JT} = 0}$$

Also,

- $\mu_{JT} = \left[\dfrac{\partial T}{\partial p}\right]_h = \dfrac{1}{C_p}\left[T\left(\dfrac{\partial v}{\partial T}\right)_p - v\right]$

- $\beta = \dfrac{1}{v}\left[\dfrac{\partial v}{\partial T}\right]_p$

$$\mu_{JT} = \dfrac{v}{C_p}[\beta T - 1]$$

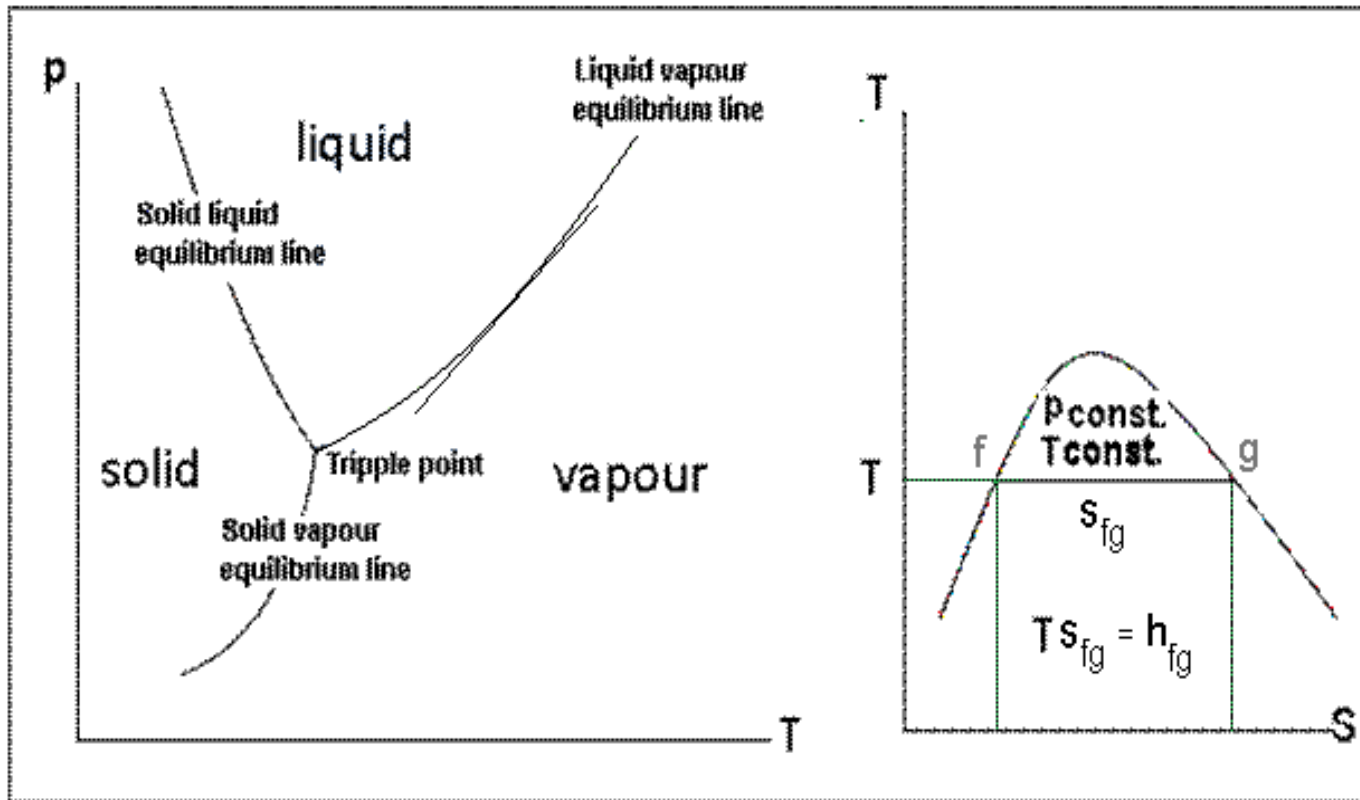*For inversion curve*

- $\mu_{JT} = \dfrac{v}{C_p}[T\beta - 1] = 0$

Since, v, C_p cannot be $= 0$

- $[T\beta - 1] = 0$

$$\boxed{T\beta = 1}$$

equation for the inversion curve

Clausius – Clapeyron Equation

- $p = p(T)$

- $\left[\dfrac{\partial p}{\partial T}\right]_v = \left[\dfrac{\partial s}{\partial v}\right]_T$

- $\dfrac{dp}{dT} = \left[\dfrac{\partial p}{\partial T}\right]_v = \left[\dfrac{\partial s}{\partial v}\right]_T = \left[\dfrac{\Delta s}{\Delta v}\right]_T = \dfrac{s_g - s_f}{v_g - v_f} = \dfrac{s_{fg}}{v_{fg}}$

$$\dfrac{dp}{dT} = \dfrac{1}{T}\left[\dfrac{h_{fg}}{v_{fg}}\right] \ldots\ldots Clapeyron\ equation$$

- *Simplification of Clapeyron equation*

- *At low pressures $v_g \gg v_f$, and thus $v_{fg} \approx v_g$*

- $v = v_g = \dfrac{RT}{p}$

- $\dfrac{dp}{dT} = \dfrac{1}{T}\left[\dfrac{h_{fg}}{v_{fg}}\right]$

$$\Rightarrow \frac{dp}{dT} = \frac{1}{T}\left[\frac{h_{fg}}{v_g}\right] = \frac{p}{T}\left[\frac{h_{fg}}{RT}\right] = \frac{h_{fg}}{R}\left[\frac{p}{T^2}\right]$$

- $$\frac{dp}{p} = \frac{h_{fg}}{R}\left[\frac{dT}{T^2}\right]$$

Integrating..

$$ln\left(\frac{p_2}{p_1}\right)_{sat} = \frac{h_{fg}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]_{sat}$$

$Clausius - Clapeyron\ equation$