$$p = \frac{RT}{v-b} - \frac{a}{v^2} \implies p_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} \quad (1)$$

$$\left.\frac{\partial p}{\partial v}\right|_T = 0 \text{ at critical state} \implies -\frac{RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0 \quad (2)$$

$$\left.\frac{\partial^2 p}{\partial v^2}\right|_T = 0 \quad \text{"} \implies \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0 \quad (3)$$

$$\text{Eq.}(2) \times \frac{2}{V_c - b} \implies -\frac{2RT_c}{(V_c-b)^3} + \frac{4a}{V_c^3(V_c-b)} = 0 \quad (4)$$

$$\text{Eq.}(3) + \text{Eq.}(4) \implies 0 - \frac{6\cancel{a}}{V_c^{\cancel{4}}} + \frac{4\cancel{a}}{\cancel{V_c^3}(V_c-b)} = 0$$

$$\implies 6(V_c - b) = 4V_c \quad \text{or} \quad 2V_c = 6b$$

$$\text{or} \quad \underline{V_c = 3b} \quad (5)$$

$$\text{Plug Eq. (5) in Eq. (2)} \implies -\frac{RT_c}{4b^{\cancel{2}}} + \frac{2a}{27b^{\cancel{3}}} = 0$$

$$\implies T_c = \frac{8a}{27Rb} \quad \text{—} \ (6)$$

Plugging Eqs. (5) and ( ) in (1) $\implies$

$$p_c = \frac{\cancel{R}\,\cancel{8}^{4}a}{27\cancel{R}b \times \cancel{2}b} - \frac{a}{9b^2}$$

$$= \frac{4a - 3a}{27b^2} = \underline{\frac{a}{27b^2}} \quad (7)$$

$P_r = p/p_c \quad p = p_r P_c \quad$ Similarly $\quad V = v_r V_c$

(2) $p_r = \frac{p}{p_c} \Rightarrow p = p_r p_c$ Similarly $V = V_r V_c$

$T = T_r T_c$

$$\text{V-W} \Longrightarrow p = \frac{RT}{(V-b)} - \frac{a}{V^2} \quad \text{with } p_c = \frac{a}{27b^2},\ V_c = 3b$$

$$T_c = \frac{8}{27}\frac{a}{bR}$$

$$\therefore \text{V-W} \Rightarrow p_r \frac{\cancel{a}}{27\cancel{b^2}} = \frac{\cancel{R} T_r}{(V_r 3\cancel{b} - \cancel{b})} \times \frac{8\cancel{a}}{27\cancel{R}\cancel{b}} - \frac{\cancel{a}}{V_r^2 9\cancel{b^2}}$$

$$\Rightarrow \frac{p_r}{\cancel{27}\,3} = \frac{T_r}{(3V_r - 1)}\frac{8}{\cancel{27}\,3} - \frac{1}{\cancel{9}V_r^2}$$

$$\Rightarrow p_r(3V_r - 1) = 8T_r - \frac{3(3V_r - 1)}{V_r^2}$$

$$\Rightarrow (3V_r - 1)\left\{p_r + \frac{3}{V_r^2}\right\} = 8T_r. \quad \text{(Ans)}$$

$$\text{or} \quad p_r = \frac{8T_r}{(3V_r - 1)} - \frac{3}{V_r^2}$$

(3) $$du = T\,ds - p\,dv$$

$$\left.\frac{\partial u}{\partial p}\right|_T = T\left.\frac{\partial s}{\partial p}\right|_T - p\left.\frac{\partial v}{\partial p}\right|_T$$

From Maxwell Relations

$$\left.\frac{\partial s}{\partial p}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_p$$

$$\therefore \left.\frac{\partial u}{\partial p}\right|_T = -T\left.\frac{\partial V}{\partial T}\right|_p - p\left.\frac{\partial v}{\partial p}\right|_T$$

(4) $$\left.\frac{\partial p}{\partial T}\right|_s = -\left.\frac{\partial p}{\partial s}\right|_T \left.\frac{\partial s}{\partial T}\right|_p$$ [Cyclic + reciprocal rules]

Maxwell $\Rightarrow$ $$-\left.\frac{\partial p}{\partial s}\right|_T = \left.\frac{\partial T}{\partial v}\right|_p$$

From Notes $$\left.\frac{\partial s}{\partial T}\right|_p = \frac{C_p}{T}$$

$$\therefore \left.\frac{\partial p}{\partial T}\right|_s = \left.\frac{\partial T}{\partial v}\right|_p \frac{C_p}{T} = \frac{C_p}{T\left.\frac{\partial v}{\partial T}\right|_p} \quad (1)$$

By definition $\beta = \frac{1}{v}\left.\frac{\partial v}{\partial T}\right|_p$

$$\Rightarrow \left.\frac{\partial v}{\partial T}\right|_p = \beta v \quad (2)$$

$\therefore$ from (1) + (2) $$\left.\frac{\partial p}{\partial T}\right|_s = \frac{C_p}{T v \beta}$$

(5) $$T\,ds = T\left\{ \frac{\partial s}{\partial T}\Big|_p dT + \frac{\partial s}{\partial p}\Big|_T dp \right\}$$

$$T \frac{\partial s}{\partial T}\Big|_p = C_p \;; \qquad \frac{\partial s}{\partial p}\Big|_T = -\frac{\partial v}{\partial T}\Big|_p$$

(Shown in class) (maxwell)

$$\Rightarrow T\,ds = C_p\,dT - T\frac{\partial v}{\partial T}\Big|_p dp \qquad (1)$$

Similarly

$$T\,ds = T\left\{ \frac{\partial s}{\partial T}\Big|_v dT + \frac{\partial s}{\partial v}\Big|_T dv \right\}$$

$$T\frac{\partial s}{\partial T}\Big|_v = C_v \;; \qquad \frac{\partial s}{\partial v}\Big|_T = \frac{\partial p}{\partial T}\Big|_v$$

$$\Rightarrow T\,ds = C_v\,dT + T\frac{\partial p}{\partial T}\Big|_v dv \qquad (2)$$

Equating (1) + (2) and rearranging

$$\Rightarrow (C_p - C_v)\,dT = T\frac{\partial p}{\partial T}\Big|_v dv + T\frac{\partial v}{\partial T}\Big|_p dp \qquad (3)$$

Expanding $dT = \frac{\partial T}{\partial v}\Big|_p dv + \frac{\partial T}{\partial p}\Big|_v dp$

and equating coefficients of (either dv or) dp leads to

$$(C_p - C_v)\frac{\partial T}{\partial p}\Big|_v \cancel{dp} = T\frac{\partial v}{\partial T}\Big|_p \cancel{dp}$$

$$\Rightarrow C_p - C_v = \frac{T\frac{\partial v}{\partial T}\Big|_p}{\frac{\partial T}{\partial p}\Big|_v} = \underline{T\frac{\partial v}{\partial T}\Big|_p \frac{\partial p}{\partial T}\Big|_v}$$

From Eq.(2) of Sol of previous problem

(6) From Eq.(2) of Sol 5, we get

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

Since ds is exact differential

$$\left.\frac{\partial \left\{\frac{C_v}{T}\right\}}{\partial v}\right|_T = \left.\frac{\partial \left\{\left.\frac{\partial p}{\partial T}\right|_v\right\}}{\partial T}\right|_v$$

$$= \left.\frac{\partial^2 p}{\partial T^2}\right|_v$$

$$\text{V-W} \rightarrow p = \frac{RT}{(v-b)} - \frac{a}{v^2}$$

$$\Rightarrow \frac{\partial^2 p}{\partial T^2} = 0$$

$\Rightarrow \frac{C_v}{T}$ is only a function of T

or C_v is only a function of T

(7) Proceeding similarly

$$\left.\frac{\partial \frac{C_p}{T}}{\partial p}\right|_T = \left.\frac{\partial^2 v}{\partial T^2}\right|_p$$

Since V-W is cubic in v,

$$\frac{C_p}{T} \neq f(T) \text{ alone}$$

But $C_v = f(T) \Rightarrow (C_p - C_v) \neq f(T)$ alone

In Problem 5, we have shown that

$$c_p - c_v = T \frac{\partial v}{\partial T}\Big|_p \frac{\partial p}{\partial T}\Big|_v$$

V-W gas $\Rightarrow$ $p = \frac{RT}{v-b} - \frac{a}{v^2}$

$$\Rightarrow \frac{\partial p}{\partial T}\Big|_v = \frac{R}{v-b} \qquad \text{— } (1)$$

Similarly V-W $\Rightarrow$ $pv^3 - (pb+RT)v^2 + av - ab = 0$

Differentiating above expression with T along p = Constant gives

$$p\,3v^2 \frac{\partial v}{\partial T}\Big|_p - pb\,2v\frac{\partial v}{\partial T}\Big|_p - RT\,2v\frac{\partial v}{\partial T}\Big|_p - Rv^2 + a\frac{\partial v}{\partial T}\Big|_p = 0$$

$$\Rightarrow \frac{\partial v}{\partial T}\Big|_p \left\{3v^2p - 2v(pb+RT) + a\right\} = Rv^2$$

$$\text{or } \frac{\partial v}{\partial T}\Big|_p = \frac{Rv^2}{\left\{3v^2p - 2v(pb+RT)+a\right\}} \qquad (2)$$

Thus $(C_p - C_v)$ is not a function of T alone

(8) Using the cyclic rule, we can write

$$\underbrace{\frac{\partial T}{\partial p}\Big|_h}_{\mu} \frac{\partial p}{\partial h}\Big|_T \underbrace{\frac{\partial h}{\partial T}\Big|_p}_{c_p} = -1$$

$$\Rightarrow \mu = \frac{-1}{c_p \frac{\partial p}{\partial h}\Big|_T} = \frac{-1}{c_p} \frac{\partial h}{\partial p}\Big|_T$$

From slide 29/44 last line

$$\frac{\partial h}{\partial p}\Big|_T = -T \frac{\partial v}{\partial T}\Big|_p + v$$

$$\Rightarrow \mu = -\frac{1}{c_p}\left\{-T\frac{\partial v}{\partial T}\Big|_p + v\right\}$$

$$= \frac{1}{c_p}\left\{T\frac{\partial v}{\partial T}\Big|_p - v\right\}$$

For ideal gas $v = \frac{RT}{p} \Rightarrow \frac{\partial v}{\partial T}\Big|_p = \frac{R}{p}$

$$\Rightarrow \mu = \frac{1}{c_p}\left\{\frac{RT}{p} - v\right\}$$

$$= \frac{1}{c_p}\left\{v - v\right\} = 0$$