ASSIGNMENT-04

MODEL SOLUTION

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6.3-2 Given;

$$P = \frac{U}{V}, \quad T = 3B\left(\frac{NV}{U^2}\right)^{-1/3}$$

→ For Throttling process;

$$\boxed{H_i = H_f} \quad — (1)$$

→ Hence, we first derive H in terms of T and V;

Using,

$$H = U + PV$$

$$\boxed{H = 2U} \quad — (2) \qquad [\because P = U/V]$$

→ Now;

$$T = 3B\left(\frac{NV}{U^2}\right)^{-1/3}$$

$$T^3 = (3B)^3\left(\frac{NV}{U^2}\right)^{-1}$$

$$\therefore T^3 = (3B)^3 \frac{UP}{N}$$

$$\therefore \frac{T^3}{P} = (3B)^3\left(\frac{U}{N}\right)$$

$$\Rightarrow \boxed{U = \frac{T^3 N}{(3B)^3 P}}$$

→ Substituting in (2), and using (1);

$$\frac{T_i^3 \cancel{N}}{\cancel{(3B)^3} P_i} = \frac{T_f^3 \cancel{N}}{\cancel{(3B)^3} P_f} \Rightarrow \boxed{T_f = T_i\left(\frac{P_f}{P_i}\right)^{1/3}}$$

6.3.3 For an ideal van der waals fluid we have

$$S = NR \ln \left\{ (v-b)\left(u+\frac{a}{v}\right)^c \right\} + NS_0 \quad \text{(1)}$$

$$\Rightarrow \quad NR \ln \left\{ (v-b) + \left(u+\frac{a}{v}\right)^c \right\} = S - NS_0$$

$$(v-b)(u+a/v)^c = \exp\left\{ \frac{S-NS_0}{NR} \right\}$$

$$(v-b)(u+a/v)^c = \exp\left\{ \frac{s-s_0}{R} \right\} \quad \left\{ \text{where } s = \frac{S}{N} \right\}$$

$$\left(u+\frac{a}{v}\right)^c = \frac{1}{v-b} \exp\left\{ \frac{s-s_0}{R} \right\}$$

$$u+\frac{a}{v} = \frac{1}{(v-b)^{1/c}} \left(\exp\left\{ \frac{s-s_0}{R} \right\} \right)^{1/c}$$

$$u = -\frac{a}{v} + \frac{1}{(v-b)^{1/c}} \exp\left\{ \frac{s-s_0}{cR} \right\} \quad \text{(2)}$$

$$\boxed{P = -\left(\frac{\partial u}{\partial v}\right)_{T,s} = -\frac{a}{v^2} + \frac{1}{c}(v-b)^{-1/c-1} \exp\left\{ \frac{s-s_0}{cR} \right\}} \quad \text{(3)}$$

& $$T = \left(\frac{\partial u}{\partial s}\right)_{T,v} = 0 + \frac{1}{CR}(v-b)^{-1/c} \exp\left\{\frac{s-s_0}{CR}\right\}$$

$$\boxed{T = \frac{1}{CR}(v-b)^{-1/c} \exp\left\{\frac{s-s_0}{CR}\right\}} \quad \text{—④}$$

$$h = u + pv$$

$\Rightarrow$

$$h = -\frac{a}{v} + (v-b)^{-1/c} \exp\left\{\frac{s-s_0}{CR}\right\} +$$
$$v\left[-\frac{a}{v^2} + \frac{1}{c}(v-b)^{-1/c-1} \exp\left\{\frac{s-s_0}{CR}\right\}\right]$$

$$h = -\frac{2a}{v} + \left[1 + \frac{v}{c(v-b)}\right](v-b)^{-1/c} \exp\left\{\frac{s-s_0}{CR}\right\}$$

from eqn 4

$$h = -\frac{2a}{v} + \left[1 + \frac{v}{c(v-b)}\right] CRT$$

$$\boxed{h = \frac{-2a}{v} + RT\left(c + \frac{v}{v-b}\right)} \quad \text{—⑤}$$

In the Joule-Thomson process

$$h_f = h_i \qquad \text{——— (5)}$$

Now, from equation (5) & (6)

$$-\frac{2a}{v_f} + RT_f\left(c+\frac{v_f}{v_f-b}\right) = \frac{-2a}{v_i} + RT_i\left(c+\frac{v_i}{v_i-b}\right)$$

$$\left(c+\frac{v_f}{v_f-b}\right)RT_f = 2a\left(\frac{1}{v_f}-\frac{1}{v_i}\right) + RT_i\left(c+\frac{v_i}{v_i-b}\right)$$

$$\boxed{T_f = \frac{1}{R\left(c+\frac{v_f}{v_f-a}\right)}\left\{2a\left(\frac{1}{v_f}-\frac{1}{v_i}\right) + RT_i\left(c+\frac{v_i}{v_i-b}\right)\right\}}$$

——— (6)

$$\frac{dT}{dP} = \frac{v}{C_p}(T\alpha - 1) \quad \text{——— (7)}$$

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

for van der waals fluid

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

$$\left(\frac{\partial P}{\partial P}\right)_P = \frac{R}{v-b}\left(\frac{\partial T}{\partial T}\right)_P + RT\left(\frac{-1}{(v-b)^2}\right)\left(\frac{\partial v}{\partial T}\right)_P + \frac{2a}{v^3}\left(\frac{\partial v}{\partial T}\right)_P$$

$$\left(\frac{2a}{v^3} - \frac{RT}{(v-b)^2}\right)\left(\frac{\partial v}{\partial T}\right)_P + \frac{R}{v-b} = 0$$

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

$$\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{v(v-b)\left(\frac{RT}{(v-b)^2} - \frac{2a}{v^3}\right)}$$

$$\alpha = \frac{R}{v\left(\frac{RT}{v-b} - \frac{2a}{v^3}(v-b)\right)}$$

$$\alpha = \frac{R}{v\left(P + \frac{a}{v^2} - \frac{2a}{v^2} + \frac{2ab}{v^3}\right)}$$

$$\alpha = \frac{R}{\left(Pv - \frac{a}{v} + \frac{2ab}{v^2}\right)}$$

In this problem, we have to neglect the $1/v^2$. so, the above equation becomes

$$\alpha = \frac{R}{Pv - \frac{a}{v}}$$

$$\alpha = \frac{R}{\frac{RTv}{v-b} - \frac{a}{v} - \frac{a}{v}}$$

$$\alpha = \frac{R}{RT\left\{\frac{1}{1-b/v} - \frac{2a}{RTv}\right\}}$$

$$\alpha = \frac{1}{T\left\{1 + \frac{b}{v} - \frac{2a}{RTv}\right\}}$$ {Apply Tylor series expansion

$$\alpha = \frac{1}{T}\left\{1 - \frac{b}{v} + \frac{2a}{RTv}\right\}$$ {Apply Tylor series expansion

Now, equation (7) becomes

$$\frac{dT}{dp} = \frac{v}{C_p}\left(T\alpha - 1\right)$$

$$= \frac{v}{C_p}\left\{1 - \frac{b}{v} + \frac{2a}{RTv} - 1\right\}$$

$$\boxed{\frac{dT}{dp} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)}$$

for CO_2

$$C_p = 29.5 \ \frac{J}{mole \cdot K}$$

$$\Delta P = 10^6 \ pa$$

$$T_{mean} = 0\ °C = 273.15\ K$$

$$a = 0.364 \ \frac{m^6\, pa}{mol^2}$$

$$b = 4.267 \times 10^{-5} \ \frac{m^3}{mol}$$

$$R = 8.314 \ \frac{J}{mole\, K}$$

$$\frac{\Delta T}{\Delta P} = \frac{1}{29.5}\left\{\frac{2 \times 0.364}{8.314 \times 273.15} - 4.267 \times 10^{-5}\right\}$$

$$\boxed{\Delta T = 9.42\ K}$$

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$\boxed{9.4-2}$ For a van der Waals system;

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

→ To find V_c, P_c & T_c we use

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

$$\therefore \left(\frac{\partial P}{\partial V}\right)_{T_c} = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3}$$

At critical state;

$$\frac{2a}{V_c^3} = \frac{RT_c}{(V_c-b)^2} \quad \text{—} \quad (1)$$

$$\rightarrow \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

At critical state;

$$\frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4} \quad \text{—} \quad (2)$$

→ Dividing eq (1) by (2);

$$\frac{\cancel{2a}}{V_c^{\cancel{3}} \cdot \frac{3\cancel{6a}}{V_c^{\cancel{4}}}} = \frac{\cancel{RT_c}}{(V_c-b)^{\cancel{2}} \cdot \frac{\cancel{2RT_c}}{(V_c-b)^{\cancel{3}}}}$$

$$\frac{V_c}{3} = \frac{V_c - b}{2}$$

$$\Rightarrow \boxed{V_c = 3b}$$

→ Substituting V_c in eq ①;

$$\frac{2a}{V_c^3} = \frac{RT_c}{(V_c - b)^2}$$

$$\frac{2a}{27b^3} = \frac{RT_c}{(2b)^2}$$

$$\therefore T_c = \frac{(2a)(4b^2)}{27b^3R}$$

$$\boxed{T_c = \frac{8a}{27Rb}}$$

→ Substituting T_c & V_c in Van der Waals EOS

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2}$$

$$= \frac{R}{(3b-b)}\left(\frac{8a}{27Rb}\right) - \frac{a}{(3b)^2}$$

$$= \frac{8aR}{(2b)(27Rb)} - \frac{a}{9b^2}$$

$$\Rightarrow \boxed{P_c = \frac{a}{27b^2}}$$