ASSIGNMENT 3

MODEL SOLUTION

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7.2.2 Given;

$$N = 1$$

$$dQ = A\,dP$$

→ As we know;

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

→ Using Maxwell relations,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{— } (1)$$

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

→ Moreover,

$$dQ = T\,dS$$

$$A\,dP = T\,dS$$

$$\therefore \boxed{\frac{dS}{dP} = \frac{A}{T}}$$

(3)

$$\Rightarrow \boxed{\alpha = -\frac{A}{TV}} \quad \text{— } (1)$$

7.2.3 Given,

$$\alpha = \frac{1}{T}$$

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

$$\therefore \boxed{\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T}} \quad \text{— } (1)$$

(1)

→ Let $N = 1$ mole

$$\left(\frac{\partial c_p}{\partial P}\right)_T = \frac{\partial}{\partial P}\left[\frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_P\right]_T$$

$$= \frac{T}{N}\frac{\partial}{\partial P}\left[\left(\frac{\partial S}{\partial T}\right)_P\right]_T$$

$$= \frac{T}{N}\frac{\partial}{\partial T}\left[\left(\frac{\partial S}{\partial P}\right)_T\right]_P$$

$$= \frac{T}{N}\frac{\partial}{\partial T}\left[-\left(\frac{\partial V}{\partial T}\right)_P\right]_P \qquad (1)$$

$$= \frac{-T}{N}\left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P\right)_P$$

$$\cancel{= -T\left[\frac{\partial V}{\partial T}\right.} \quad = -T\left[\frac{\partial}{\partial T}\left(\frac{V}{T}\right)\right]_P$$

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

$$= -T\left[\frac{1}{T}\left(\frac{V}{T}\right) - \frac{V}{T^2}\right] \qquad \text{[From (1)]}$$

$$= -T\left[\frac{V}{T^2} - \frac{V}{T^2}\right]$$

$$\boxed{\left(\frac{\partial c_p}{\partial P}\right)_T = 0} \qquad (2)$$

Hence proved.

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7.3-5

$$\left(\frac{\partial s}{\partial f}\right)_V = \frac{[s, v]}{[f, v]}$$

Using $[f, V] = -s[T, V] - P\cancel{[V, V]}^{\to 0}$ — 1

$$\therefore \left(\frac{\partial s}{\partial f}\right)_V = \frac{[s, V]}{-s[T, V]}$$

$$= \frac{1}{(-s)\frac{[T, V]}{[s, V]}}$$ — 1

As we know,

$$\frac{C_v}{T} = \frac{[s, V]}{[T, V]}$$

$$\therefore \left(\frac{\partial s}{\partial f}\right)_V = \frac{C_v}{-s \cdot T}$$ — 1

Now, $$S = \int_{T_0}^{T} \left(\frac{C_p}{T}\right)_{P_0} dT - \int_{P_0}^{P} (\alpha V)_{T_0} dP + S_0$$

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$\boxed{7.4\text{-}5}$ $-\frac{dV}{V} = 0.01$, S = constant

$\rightarrow \left(\frac{\partial u}{\partial V}\right)_S dV = du$

→ Using gibbs duhem eq^n ;

$$\left(\frac{\partial u}{\partial V}\right)_S = \frac{\partial}{\partial V}\left[(-S\,\partial T)\right]_S + \frac{\partial}{\partial V}\left[V\,dP\right]_S \quad \text{— (1)}$$

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

$$= -S\frac{[T,S]}{[V,S]} + V\frac{[P,S]}{[V,S]}$$

$$= \frac{-S\cdot -[V,P]}{[V,S]} + V\frac{1}{\frac{[V,S]}{[P,S]}} \qquad \left\{\because [T,S] = -[V,P]\right\} \text{ (1)}$$

$$= \frac{S\cdot\alpha V[T,P]}{-k_S\cdot V[P,S]} + V\frac{1}{(-k_S\cdot V)}$$

$$= \frac{S\alpha[T,P]}{k_S[S,P]} - \frac{1}{k_S} \qquad \left[\because k_S = -\frac{1}{V}\cdot\frac{[V,S]}{[P,S]}\right]$$

$$= \frac{S\alpha}{k_S\frac{[S,P]}{[T,P]}} - \frac{1}{k_S}$$

$$= \frac{S\alpha}{k_S\left(\frac{C_P}{T}\right)} - \frac{1}{k_S}$$

$$\therefore du = \left(\frac{S\alpha T}{k_S C_P} - \frac{1}{k_S}\right)\cdot dV$$

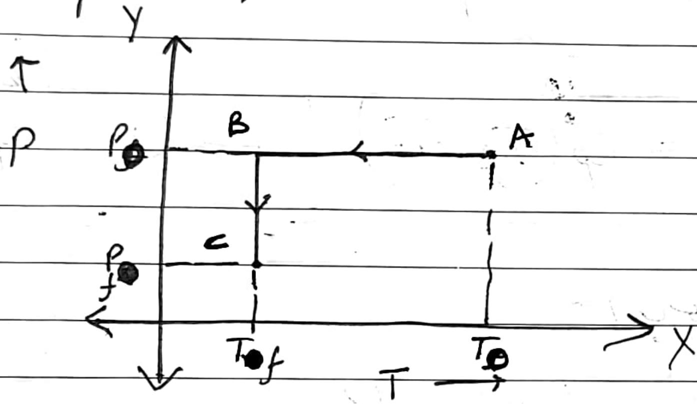
$$\boxed{du = \left(\frac{1}{k_S}\right)\left[\frac{S\alpha T}{C_P} - 1\right]\cdot(-0.01V)}$$

(4)

$$\boxed{dU = \frac{1}{\left(K_T - \frac{V\alpha^2 T}{C_p}\right)} \left(\frac{S\alpha T}{C_p} - 1\right)\left(-0.07\, V\right)} \quad \text{--- (2)}$$

$$\boxed{\because K_S = K_T - \frac{V\alpha^2 T}{C_p}}$$

7-4-24 The throttling process can be divided into two processes as shown below :-



A→B is Isobaric
B→C is Isothermal

→ Moreover, in a throttling process the Enthalpy remains constant

$$\therefore \boxed{\Delta H_1 + \Delta H_2 = 0} \quad \text{--- (1)}$$

→ Process A→B :-

$$dH_1 = \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$= \frac{[H, P]}{[T, P]} dT$$

$$= \left\{\frac{T[S, P] + \cancel{V[P, P]}^{\,0}}{[T, P]}\right\} dT$$

$$dH_1 = \frac{T[S, P]}{[T, P]} dT$$

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$$\left[\because \frac{C_p}{T} = \frac{[S,P]}{[T,P]}\right]$$

$$\therefore dH_1 = \cancel{T}\,\frac{C_p}{\cancel{T}}\,dT$$

$$dH_1 = C_p\,dT$$

→ Integrating,

$$\Delta H_1 = \int_{T_0}^{T_f} C_p\,dT$$

$$\boxed{\Delta H_1 = C_p^\circ(T_f - T_0)} \quad — (2) \quad — (3)$$

[along Isobar $C_p = C_p^\circ$]

→ Process Block

$$dH_2 = \left(\frac{\partial H}{\partial P}\right)_T \cdot dP$$

$$= \frac{[H,T]}{[P,T]}\,dP$$

$$= \left\{\frac{T[S,T] + V[P,T]}{[P,T]}\right\} dP$$

$$= \left\{\frac{T[S,T]}{[P,T]} + V\,\cancel{\frac{[P,T]}{[P,T]}}^{\,1}\right\} dP$$

$$= \left\{\frac{T[V,P]}{[P,T]} + V\right\} dP \quad — (1) \quad \left[\because [S,T] = [V,P]\right]$$

$$= \left\{\frac{-T[V,P]}{[T,P]} + V\right\} dP$$

$$= \left\{-T(\alpha V) + V\right\} dP \qquad \left[\because \alpha = \frac{1}{V}\frac{[V,P]}{[T,P]}\right]$$

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$$\therefore \boxed{dH_2 = (1 - T_0\alpha_0) \cdot V\,dP} \quad — (3)$$ [along isotherm $T = T_0,\ \alpha = \alpha_0$]

→ <u>Now</u>, we need volume in terms of pressure

$$V = V(P)$$

$$\therefore dV = \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$= \frac{[V,T]}{[P,T]} \cdot dP$$

$$= -VK_T\,dP.$$

$$\therefore dV = -\cancel{V}\frac{A}{V^{\cancel{2}}}\,dP$$ [along isotherm $K_T = A/V^2,\ A > 0$]

$$\therefore -\int_{V_0}^{V} V\,dV = \int_{P_0}^{P} A\,dP$$

$$\therefore -\left[\frac{V^2}{2}\right]_{V_0}^{V} = A\left[P\right]_{P_0}^{P} \Rightarrow \boxed{V^2 - V_0^2 = -2A(P - P_0)}$$

(1)

→ <u>Substituting in eq (3)</u>;

$$dH_2 = (1 - T_0\alpha_0) \cdot \left[V_0^2 - 2A(P - P_0)\right]^{1/2} dP$$

$$\Delta H_2 = (1 - \alpha_0 T_0) \cdot \int_{P_0}^{P_f} \left[V_0^2 - 2A(P - P_0)\right]^{1/2} \cdot dP$$

$$= (1 - \alpha_0 T_0) \cdot \left[\frac{\left[V_0^2 - 2A(P - P_0)\right]^{3/2}}{\frac{3}{2} \cdot (-2A)}\right]_{P_0}^{P_f}$$

$$= \frac{(1 - \alpha_0 T_0)}{-3A} \left\{\left[V_0^2 - 2A(P_f - P_0)\right]^{3/2} - \left[V_0^2\right]^{3/2}\right\}$$

$$\boxed{\Delta H_2 = \left(\frac{\alpha_0 T_0 - 1}{3A}\right) \left\{\left[V_0^2 - 2A(P_f - P_0)\right]^{3/2} - V_0^3\right\}} \quad — (4)$$

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→ Substituting ② & ④ in ①;

$$C_p^0 (T_f - T_0) + \frac{(\alpha_0 T_0 - 1)}{3A} \left\{ \left[V_0^2 - 2A(P_f - P_0) \right]^{3/2} - V_0^3 \right\} = 0$$

$$\therefore \boxed{T_f = T_0 - \frac{(\alpha_0 T_0 - 1)}{3AC_p^0} \left\{ \left[V_0^2 - 2A(P_f - P_0) \right]^{3/2} - V_0^3 \right\}}$$

— ①

→ In order to get $T_f < T_0$;

$$T_0 - \frac{(\alpha_0 T_0 - 1)}{3AC_p^0} \left\{ \left[V_0^2 - 2A(P_f - P_0) \right]^{3/2} - V_0^3 \right\} < T_0$$

$$\therefore \frac{(\alpha_0 T_0 - 1)}{3AC_p^0} \left\{ \left[V_0^2 - 2A(P_f - P_0) \right]^{3/2} - V_0^3 \right\} > 0$$

Since $A > 0$,

$$(\alpha_0 T_0 - 1) \underbrace{\left\{ \left[V_0^2 - 2A(P_f - P_0) \right]^{3/2} - V_0^3 \right\}}_{<0} > 0$$

$$\therefore \alpha_0 T_0 - 1 < 0$$

$$\Rightarrow \boxed{\alpha_0 T_0 < 1} \quad — ②$$

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