

5.3-7.  $H = AS^2 N^{-1} \log(P/P_0)$

From  $dH = Tds + vdp + \mu dN$

①  $(\frac{\partial H}{\partial P})_{S,N} = v = \frac{AS^2 N^{-1}}{P}$  , ②  $(\frac{\partial H}{\partial S})_{P,N} = T = 2ASN^{-1} \log(P/P_0)$

Eliminate  $P$  using ① & ②

$$T = 2ASN^{-1} \log \frac{AS^2 N^{-1}}{P_0 v}$$

Differentiate with  $T$  at constant  $v$

$$1 = 2AN^{-1} \left(\frac{\partial S}{\partial T}\right)_v \log \frac{AS^2 N^{-1}}{P_0 v} + 2ASN^{-1} \cdot 2 \frac{1}{S} \left(\frac{\partial S}{\partial T}\right)_v$$

$$= \ln P/P_0$$

Since  $C_v = \frac{T}{N} \left(\frac{\partial S}{\partial T}\right)_v$

$$C_v = \left[ \frac{2A}{T} \log(P/P_0) + \frac{4A}{T} \right]^{-1}$$

5.3-12

$$(s-s_0)^4 = Avu^2$$

$$u = A^{-\frac{1}{2}} v^{-\frac{1}{2}} (s-s_0)^2$$

$$\Rightarrow \left\{ \begin{array}{l} \left(\frac{\partial u}{\partial s}\right)_v = T = 2A^{-\frac{1}{2}} v^{-\frac{1}{2}} (s-s_0) \\ -\left(\frac{\partial u}{\partial v}\right)_s = p = \frac{1}{2} A^{-\frac{1}{2}} v^{-\frac{3}{2}} (s-s_0)^2 \end{array} \right\} \Rightarrow \frac{T^2}{p} = 8A^{-\frac{1}{2}} v^{\frac{1}{2}}$$

Legendre transform to  $g (\equiv G/N)$

$$g = u - Ts + pV = \frac{1}{4} A^{\frac{1}{2}} v^{\frac{1}{2}} T^2 + \frac{1}{8} A^{\frac{1}{2}} v^{\frac{1}{2}} T^2 - \frac{1}{2} T^2 A^{\frac{1}{2}} v^{\frac{1}{2}} - Ts_0$$

$$= -\frac{A^{\frac{1}{2}}}{8} T^2 v^{\frac{1}{2}} - Ts_0 = -\frac{A}{64} T^4 / p - Ts_0$$

$$u = \frac{3}{2} p v, \quad p = A v T^4$$

$$\frac{1}{T} = \left(\frac{3}{2}\right)^{\frac{1}{4}} A^{\frac{1}{4}} u^{-\frac{1}{4}} v^{\frac{1}{2}}, \quad \frac{p}{T} = \frac{2}{3} \left(\frac{3}{2}\right)^{\frac{1}{4}} A^{\frac{1}{4}} u^{\frac{3}{4}} v^{-\frac{1}{2}}$$

f. eq  $\rightarrow$

$$dS = \frac{1}{T} du + \frac{p}{T} dv = \left(\frac{3}{2}\right)^{\frac{1}{4}} A^{\frac{1}{4}} d\left(\frac{4}{3} u^{\frac{3}{4}} v^{\frac{1}{2}}\right)$$

$$S = \left(\frac{3}{2}\right)^{\frac{1}{4}} A^{\frac{1}{4}} \cdot \frac{4}{3} u^{\frac{3}{4}} v^{\frac{1}{2}} + S_0$$

$$u = u(S, v) = \left[\frac{3}{4} \left(\frac{3}{2}\right)^{-\frac{1}{4}}\right]^{\frac{4}{3}} A^{-\frac{1}{3}} S^{\frac{4}{3}} v^{-\frac{2}{3}}$$

$$T = \left(\frac{\partial u}{\partial S}\right)_v = \frac{4}{3} u \cdot S^{-1} \rightarrow u = \frac{3}{4} TS$$

$$-p = \left(\frac{\partial u}{\partial v}\right)_S = -\frac{2}{3} u \cdot v^{-1} \rightarrow u = \frac{3}{2} p v$$

$$f = f(T, v) = u - TS = +\frac{3}{4} TS - TS = -\frac{1}{4} TS = -\frac{1}{3} u = -\frac{1}{2} p v$$

$$\text{Since } p = A v T^4 \rightarrow p v = A v^2 T^4$$

$$\therefore f(T, v) = -\frac{1}{2} A v^2 T^4$$

$$g = g(T, p) = u - TS + p v = \frac{1}{2} p v$$

$$\text{Using } p = A v T^4, \text{ we get } v = A^{-1} p T^{-4}$$

$$\therefore g(T, p) = \frac{1}{2} p \cdot A^{-1} p T^{-4} = \frac{p^2}{2 A T^4}$$

7.2.-3.  $\alpha = \frac{1}{T}$  then  $\left(\frac{\partial G}{\partial P}\right)_T = ?$

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

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

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

$V\alpha = V/T$

$$\therefore \alpha = \frac{1}{T} \rightarrow \left(\frac{\partial G}{\partial P}\right)_T = 0$$

7.3.-1.

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$T dS = T \left(\frac{\partial S}{\partial T}\right)_P dT + T \left(\frac{\partial S}{\partial P}\right)_T dP$$

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

$$= N C_p dT - VT \alpha dP$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial P}\right)_T dP \rightarrow \left(\frac{\partial P}{\partial T}\right)_V = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\alpha}{\kappa_T}$$

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

$$= N C_v dT + T \cdot \frac{\alpha}{\kappa_T} dV = \alpha / \kappa_T$$

7.3.-2.

$$T \left(\frac{\partial S}{\partial T}\right)_V = N C_v - VT \alpha \left(\frac{\partial P}{\partial T}\right)_V$$

$$N C_v = N C_p - \frac{VT \alpha^2}{\kappa_T}$$

$$C_p - C_v = \frac{VT \alpha^2}{\kappa_T}$$

7.3-3.

$$\begin{aligned} \left(\frac{\partial H}{\partial V}\right)_{T,N} &= T \left(\frac{\partial S}{\partial V}\right)_{T,N} + V \left(\frac{\partial P}{\partial V}\right)_{T,N} \\ &= T \cdot \underbrace{\left(\frac{\partial P}{\partial T}\right)_V}_{\equiv \frac{\alpha}{K_T}} = \frac{T\alpha}{K_T} \end{aligned}$$

7.4-6.

$$\left(\frac{\partial H}{\partial V}\right)_U = ?$$

↳ free expansion

$$\begin{aligned} \left(\frac{\partial H}{\partial V}\right)_U &= T \left(\frac{\partial S}{\partial V}\right)_U + P \left(\frac{\partial U}{\partial V}\right)_U \\ &= T \cdot \frac{\left(\frac{\partial H}{\partial V}\right)_S}{\left(\frac{\partial U}{\partial S}\right)_V} + P \cdot \frac{\left(\frac{\partial H}{\partial V}\right)_P}{\left(\frac{\partial U}{\partial P}\right)_V} \\ &= T \cdot \frac{P}{T} + V \cdot \left\{ - \frac{\left(\frac{\partial U}{\partial V}\right)_P}{\left(\frac{\partial P}{\partial V}\right)_V} \right\} \\ &= P + V \cdot \left\{ - \frac{T \left(\frac{\partial S}{\partial V}\right)_P - P}{T \left(\frac{\partial P}{\partial V}\right)_V} \right\} \\ &= P + V \cdot \left\{ - \frac{T \left(\frac{\partial S}{\partial T}\right)_P / \left(\frac{\partial V}{\partial T}\right)_P - P}{T \cdot \frac{\left(\frac{\partial S}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial T}\right)_V}} \right\} \\ &= P + V \cdot \left\{ - \frac{(C_p / V\alpha) - P}{C_v / (\alpha / K_T)} \right\} = P - \frac{C_p / \alpha - PV}{C_v K_T / \alpha} \\ &= P - \frac{C_p - PV\alpha}{\left(C_v - \frac{TV\alpha^2}{K_T}\right) K_T} \\ &= P - \frac{C_p - PV\alpha}{C_v K_T - TV\alpha^2} \end{aligned}$$

$$7.4-7 \quad \left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial}{\partial V} \left( T \left(\frac{\partial S}{\partial T}\right)_V \right)_T = T \left[ \frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V}\right)_T \right]_V$$

$$= T \cdot \frac{\partial}{\partial T} \left(\frac{\partial P}{\partial T}\right)_V = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V = T \cdot \frac{\partial}{\partial T} \left[ \frac{R}{V-b} \right] = 0$$

$$7.4-8. \quad \left(\frac{\partial C_P}{\partial P}\right)_T = \frac{\partial}{\partial P} \left[ T \left(\frac{\partial S}{\partial T}\right)_P \right]_T \quad \text{vdw}$$

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

$$= T \cdot \frac{\partial}{\partial T} \left[ - \left(\frac{\partial V}{\partial T}\right)_P \right]_P = -T \left(\frac{\partial}{\partial T} V \alpha\right)_P$$

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

$$\text{for } P \left( V + \frac{A}{T^2} \right) = RT$$

$$P \left[ \left(\frac{\partial V}{\partial T}\right)_P - 2A \frac{1}{T^3} \right] = R.$$

$$\therefore \alpha = \left( \frac{R}{P} + 2A/T^3 \right) \frac{1}{V}$$

$$= \left( \frac{V}{T} + \frac{A}{T^3} + \frac{2A}{T^3} \right) \frac{1}{V}$$

$$= \frac{1}{T} + \frac{3A}{VT^3} \rightarrow \left(\frac{\partial \alpha}{\partial T}\right)_P = -\frac{1}{T^2} - \frac{9A}{T^4 V}$$

$$= -\frac{1}{T} \left[ \frac{1}{T} + \frac{3A}{VT^3} \right] - \frac{6A}{VT^4} - \frac{3A}{VT^3} \alpha$$

$$P\left(v + \frac{A}{T^2}\right) = RT$$

$$v = \frac{RT}{P} - \frac{A}{T^2}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} + \frac{2A}{T^3}$$

$$\alpha = \frac{R}{Pv} + \frac{2A}{T^3} \frac{1}{v}$$

$$\left(\frac{\partial \alpha}{\partial T}\right)_P = -\frac{R}{Pv^2} \left(\frac{\partial v}{\partial T}\right)_P - \frac{6A}{T^4} \frac{1}{v} - \frac{2A}{v^2 T^3} \left(\frac{\partial v}{\partial T}\right)_P$$

$$= -\frac{R}{Pv} \alpha - \frac{6A}{T^4 v} - \frac{2A}{v^2 T^3} \alpha$$

$$= -\frac{1}{v} \left( \frac{R}{P} + \frac{2A}{T^3} \right) \alpha - \frac{6A}{T^4 v}$$

$$\therefore \alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_P = -\frac{6A}{T^4 v}$$

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = -Tv \left[ \alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_P \right] = \frac{6A}{T^3}$$