3.3-1. $T = \frac{3As^2}{v}$, $p = \frac{As^3}{v^2}$ $\rightarrow$ $T = T(s, v)$

$p = p(s, v)$

$\hookrightarrow$ function of s & v

(a)

From Gibbs-Duhem relation ($d\mu = -s\,dT + v\,dp$)

One can obtain $\mu = \mu(s, v)$

Insert $T = T(s, v)$ & $p = p(s, v)$ into

$$d\mu = -s\,d\left(\frac{3As^2}{v}\right) + v\,d\left(\frac{As^3}{v^2}\right)$$

$$= -s\left(\frac{6As}{v}ds - \frac{3As^2}{v^2}dv\right) + v\left(\frac{3As^2}{v^2}ds - \frac{3As^3}{v^3}dv\right)$$

$$= -\frac{3As^2}{v}ds$$

$$\therefore \mu = \mu_0 - \frac{As^3}{v}$$

Now we have $\boxed{\mu = \mu(s, v),\ T = T(s, v),\ p = p(s, v)}$ $\rightarrow$ all intensive parameters

Therefore, it is easy to get fundamental Eq.

Use Euler equation.

plug them into

$$U = TS - pV + \mu N \Rightarrow u = Ts - pv + \mu$$

$$U/N = u = \frac{3As^2}{v}s - \frac{As^3}{v^2}v + \left(\mu_0 - \frac{As^3}{v}\right) = \mu_0 + A\frac{s^3}{v}$$

$$\therefore U = N\mu_0 + A\frac{S^3}{VN} = U_0 + A\frac{S^3}{VN}$$

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

$$= \frac{3As^2}{v}ds - \frac{As^3}{v^2}dv = A\,d\left(\frac{s^3}{v}\right)$$

$$\therefore U = U_0 + A\frac{S^3}{NV}$$

3.3-2. ① $U = PV$, ② $P = BT^2$ fundamental Eq?

Note that we have two extensive variables (U.V) available in the two equations of state

$\Rightarrow$ Fundamental Eq should be in entropy representation

from ②,①

$$\left.\begin{aligned} \frac{1}{T} &= \sqrt{B}\, U^{-1/2} V^{1/2} \\ \frac{P}{T} &= \sqrt{B}\, U^{1/2} V^{-1/2} \end{aligned}\right\} \Rightarrow dS = \frac{1}{T}dU + \frac{P}{T}dV$$

$$= \sqrt{B}\left(U^{-1/2} V^{1/2} dU + U^{1/2} V^{-1/2} dV\right)$$

$$= \sqrt{B}\, d\left[2U^{1/2}V^{1/2}\right]$$

$$\therefore\ S = NS_0 + 2\sqrt{B}\, U^{1/2} V^{1/2}$$

3.3-3 $$P = -\frac{NU}{NV - 2AVU} = -\frac{u}{v - 2Auv}$$

$$T = 2C \frac{U^{1/2} V^{1/2}}{N - 2AU} e^{AU/N} = 2C \frac{u^{1/2} v^{1/2}}{1 - 2Au} e^{Au}$$

$$\left\{\begin{aligned} \frac{P}{T} &= -\frac{1}{2C} u^{1/2} v^{-3/2} e^{-Au} \\ \frac{1}{T} &= \frac{1}{2C} u^{-1/2} v^{-1/2} e^{-Au} - \frac{1}{C} A e^{-Au} \cdot u^{1/2} v^{-1/2} \end{aligned}\right.$$

$$dS = \frac{1}{T}du + \frac{P}{T}dv$$

$$= \frac{1}{C}\left[\left(\frac{1}{2}u^{-1/2} - Au^{1/2}\right)e^{-Au} v^{-1/2} du + \left(-\frac{1}{2}\right) u^{\frac{1}{2}} v^{-\frac{3}{2}} e^{-Au} dv\right]$$

$$= \frac{1}{C} d\left[u^{\frac{1}{2}} v^{-\frac{1}{2}} e^{-Au}\right]$$

$$\therefore\ S = NS_0 + \frac{N}{C}\frac{U^{1/2}}{V^{1/2}} e^{-AU/N}$$

3.3-4. $u = \frac{3}{2}Pv$, $u^{1/2} = BTv^{1/3}$

$$\Rightarrow \quad \frac{1}{T} = B u^{-\frac{1}{2}} v^{\frac{1}{3}}$$

$$\frac{P}{T} = \frac{2}{3} B u^{\frac{1}{2}} v^{-\frac{2}{3}}$$

$$\left\{ \begin{aligned} ds &= \frac{1}{T}du + \frac{P}{T}dv \\ &= B u^{-\frac{1}{2}} v^{\frac{1}{3}} du + \frac{2}{3} B u^{\frac{1}{2}} v^{-\frac{2}{3}} dv \\ &= B\, d\left[2 u^{\frac{1}{2}} v^{\frac{1}{3}}\right] \end{aligned} \right.$$

$$\therefore \quad S = N s_0 + 2B\, U^{\frac{1}{2}} V^{\frac{1}{3}} N^{\frac{1}{6}}$$

3.4-2. from fundamental eqn.

$$S = S_0 + R \ln\left(\frac{u}{u_0}\right)^c \left(\frac{v}{v_0}\right)$$

quasi-static adiabatic process $\Rightarrow$ $đQ = TdS = 0$

$$S = \text{constant}.$$

$$\therefore \quad \left(\frac{u}{u_0}\right)^c \left(\frac{v}{v_0}\right) = e^{(S-S_0)/R} = \text{constant}$$

For ideal (monatomic) gas

$$u = \frac{3}{2}RT = \frac{3}{2}Pv$$

$$\therefore \quad \left(\frac{Pv}{P_0 v_0}\right)^c \left(\frac{v}{v_0}\right) = e^{(S-S_0)/R}$$

$$\Rightarrow \quad P v^{\frac{c+1}{c}} = \left(P_0 v_0^{\frac{c+1}{c}} e^{-\frac{1}{c} S_0/R}\right) e^{\frac{S_0}{cR}} = \text{constant}$$

where $c = 3/2$

$$\parallel$$

$$P v^{5/3} = \text{constant}$$

loci of adiabatic processes

3.4-5. $T = \left(\frac{V}{V_0}\right)^{\eta} T_0$

(a)

$$W = -\int_{V_0}^{V_1} p\,dV = -\int_{V_0}^{V} \frac{NRT}{V}\,dV$$

$$= -NRT_0 \int_{V_0}^{V_1} \left(\frac{V}{V_0}\right)^{\eta} \frac{1}{V}\,dV = -NRT_0 \int_{1}^{V_1/V_0} \left(\frac{V}{V_0}\right)^{\eta-1} d\left(\frac{V}{V_0}\right)$$

$$= -NRT_0 \frac{1}{\eta}\left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right]$$

(b) $\Delta U = \frac{3}{2} NR\Delta T = \frac{3}{2} NR(T_1 - T_0) = \frac{3}{2} NR\left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right] T_0$

(c) $Q = \Delta U - W = \frac{3}{2} NRT_0\left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right] + NRT_0 \frac{1}{\eta}\left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right]$

$$= \left(\frac{3}{2} + \frac{1}{\eta}\right) NRT_0 \left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right]$$

(d) $dQ = TdS = dU + p\,dV$

$$Q = \int dU + \underbrace{\int p\,dV}_{-W \text{ (we have already calculated in (a))}}$$

$$= \frac{3}{2} NR \int dT + NRT_0 \frac{1}{\eta}\left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right]$$

$$\left(dT = \frac{\eta T_0}{V_0^{\eta}} V^{\eta-1}\,dV \right)$$

$$= \frac{3}{2} NR \int_{V_0}^{V_1} \frac{\eta T_0}{V_0^{\eta}} V^{\eta-1}\,dV + NRT_0 \frac{1}{\eta}\left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right]$$

$$= \frac{3}{2} NRT_0 \left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right] + NRT_0 \frac{1}{\eta}\left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right]$$

$$= \cancel{\tfrac{3}{2} NR} \left(\frac{3}{2} + \frac{1}{\eta}\right) NRT_0 \left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right]$$

(e) if $\eta = -\frac{2}{3}$ then $Q = 0$

$\eta = -\frac{2}{3}$ corresponds to $T = \left(\frac{V}{V_0}\right)^{-\frac{2}{3}} T_0 \Leftrightarrow \boxed{T^{3/2} V = T_0^{3/2} V_0}$

This is equivalent to $\underline{pV^{5/3} = p_0 V_0^{5/3} = \text{const}.}$

(prob. 3.4-2)

3.5-4. $\boxed{p = \frac{NRT}{V-Nb} - \frac{N^2 a}{V^2}}$ $\quad T = \left(\frac{V}{V_0}\right)^{-\frac{1}{2}} T_0$

(a)

$$W = -\int_{V_0}^{V_1} p\,dV = -\int_{V_0}^{V_1} \left\{ \frac{NRT_0}{V-Nb}\left(\frac{V}{V_0}\right)^{-\frac{1}{2}} - \frac{N^2}{V^2}a \right\} dV$$

$$= -\frac{NRT_0}{(V_0)^{-\frac{1}{2}}} \underbrace{\int_{V_0}^{V_1} \frac{V^{-\frac{1}{2}}}{V-Nb}\,dV}_{1} + \underbrace{\int_{V_0}^{V_1} \frac{N^2}{V^2} a\,dV}_{2}$$

1 $$\int_{\sqrt{V_0}}^{\sqrt{V_1}} \frac{2\,d\sqrt{V}}{(\sqrt{V}-\sqrt{Nb})(\sqrt{V}+\sqrt{Nb})}$$

$$= \int_{\sqrt{V_0}}^{\sqrt{V_1}} \left[\frac{d\sqrt{V}}{\sqrt{V}-\sqrt{Nb}} - \frac{d\sqrt{V}}{\sqrt{V}+\sqrt{Nb}} \right] \frac{1}{\sqrt{Nb}}$$

$$= \left[\frac{1}{\sqrt{Nb}} \log\left(\frac{\sqrt{V}-\sqrt{Nb}}{\sqrt{V}+\sqrt{Nb}} \right) \right]_{\sqrt{V}=\sqrt{V_0}}^{\sqrt{V}=\sqrt{V_1}}$$

$$= \frac{1}{\sqrt{Nb}} \cdot \log\left[\left(\frac{\sqrt{V_1}-\sqrt{Nb}}{\sqrt{V_1}+\sqrt{Nb}} \right) \Big/ \left(\frac{\sqrt{V_0}-\sqrt{Nb}}{\sqrt{V_0}+\sqrt{Nb}} \right) \right]$$

2 $$-N^2 a \left[\frac{1}{V} \right]_{V_0}^{V_1} = -N^2 a \left(\frac{1}{V_1} - \frac{1}{V_0} \right)$$

$$\therefore W = -NRT_0 \sqrt{\frac{V_0}{Nb}} \left[\log\left(\frac{\sqrt{V_1}-\sqrt{Nb}}{\sqrt{V_0}-\sqrt{Nb}} \right) - \log\left(\frac{\sqrt{V_1}+\sqrt{Nb}}{\sqrt{V_0}+\sqrt{Nb}} \right) \right]$$
$$- N^2 a \left[\frac{1}{V_1} - \frac{1}{V_0} \right]$$

(b) $$\Delta U = \Delta\left(cNRT - \frac{aN^2}{V}\right) \qquad \left(\leftarrow u = cRT - \frac{a}{v}, \quad U = cNRT - \frac{aN^2}{V}\right)$$

$$= \overset{3/2}{c}NR\Delta T - aN^2\Delta\left(\frac{1}{V}\right)$$

$$= \frac{3}{2}NR\left[\left(\frac{V_1}{V_0}\right)^{-\frac{1}{2}} - 1\right]T_0 - aN^2\left(\frac{1}{V_1} - \frac{1}{V_0}\right)$$

(c) $$Q = \Delta U - W$$

$$= \frac{3}{2}NR\left[\left(\frac{V_1}{V_0}\right)^{-\frac{1}{2}} - 1\right]T_0 \cancel{- aN^2\left(\frac{1}{V_1} - \frac{1}{V_0}\right)}$$

$$+ \frac{1}{2}NRT_0\sqrt{\frac{V_0}{Nb}}\left[\log\left(\frac{\sqrt{V_1} - \sqrt{Nb}}{\sqrt{V_1} - \sqrt{Nb}}\right) - \log\left(\frac{\sqrt{V_1} + \sqrt{Nb}}{\sqrt{V_0} - \sqrt{Nb}}\right)\right]$$

$$\cancel{+ N^2a\left[\frac{1}{V_1} - \frac{1}{V_0}\right]}$$

$$= \frac{3}{2}NRT_0\left[\left(\left(\frac{V_1}{V_0}\right)^{-\frac{1}{2}} - 1\right) + \frac{1}{3}\sqrt{\frac{V_0}{Nb}}\left\{\log\left(\frac{-}{-}\right) - \log\left(\frac{+}{+}\right)\right\}\right]$$

Incidentally,

$$\sqrt{\frac{V_0}{Nb}}\left[\log\left(\frac{1 - \sqrt{\frac{Nb}{V_1}}}{1 + \sqrt{\frac{Nb}{V_1}}}\right) - \log\left(\frac{1 - \sqrt{Nb/V_0}}{1 + \sqrt{Nb/V_0}}\right)\right]$$

$$\approx \sqrt{\frac{V_0}{Nb}}\left(-2\sqrt{\frac{Nb}{V_1}} + 2\sqrt{\frac{Nb}{V_0}}\right) \quad \left(\text{when } V_1/N \gg b, \; V_0/N \gg b\right)$$

$$= 2\left(1 - \sqrt{\frac{V_0}{V_1}}\right)$$

as $a, b \to 0$

$$W = -NRT_0 \cdot 2\left(1 - \sqrt{\frac{V_0}{V_1}}\right) = 2NRT_0\left[\left(\frac{V_1}{V_0}\right)^{-\frac{1}{2}} - 1\right]$$

✓ $W = 2NRT_0 \left[\left(\frac{V_1}{V_0}\right)^{-\frac{1}{2}} - 1 \right]$ can be obtained by setting

$\eta = -\frac{1}{2}$ in the solution of 3.4-5 (a)

$$W = -NRT_0 \frac{1}{\eta} \left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1 \right]$$

$$= 2NRT_0 \left[\left(\frac{V_1}{V_0}\right)^{-\frac{1}{2}} - 1 \right]$$

from the solution of 3.4-5 (b)

✓ $\Delta U = \frac{3}{2} NR \left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1 \right] T_0$

when $\eta = -\frac{1}{2}$

$$\Delta U = \frac{3}{2} NR \left[\left(\frac{V_1}{V_0}\right)^{-\frac{1}{2}} - 1 \right] T_0 \xleftarrow{a \to 0} \frac{3}{2} NR \left[\left(\frac{V_1}{V_0}\right)^{-\frac{1}{2}} - 1 \right] T_0 - aN^2 \left[\frac{1}{V_1} - \frac{1}{V_0} \right]$$

✓ $Q = \Delta U - W = -\frac{1}{2} NRT_0 \left[\left(\frac{V_1}{V_0}\right)^{-\frac{1}{2}} - 1 \right]$ from the above result, which also agrees with

$$\left(\frac{3}{2} + \frac{1}{\eta}\right) NRT_0 \left[\left(\frac{V_1}{V_0}\right)^{-\frac{1}{2}} - 1 \right] \text{ with } \eta = -\frac{1}{2}$$

3.5-1.

(a) $u = aPv,\quad Pv^2 = bT.$

$$\rightarrow \quad \frac{1}{T} = ab\,v^{-1}u^{-1} \qquad \frac{P}{T} = b\,v^{-2}$$

$$\frac{\partial}{\partial v}\left(\frac{1}{T}\right)_u \neq \frac{\partial}{\partial u}\left(\frac{P}{T}\right)_v = 0$$

(b) $u = aPv^2 \quad Pv^2 = bT$

$$\frac{1}{T} = \frac{ab}{u} \qquad \frac{P}{T} = b\,v^{-2}$$

$$\frac{\partial}{\partial v}\left(\frac{1}{T}\right)_u = 0 = \frac{\partial}{\partial u}\left(\frac{P}{T}\right) = 0$$

$$ds = \frac{1}{T}du + \frac{P}{T}dv = \frac{ab}{u}du + bv^{-2}dv$$

$$S = Ns_0 + Nab \ln\frac{u}{u_0} - N\left(\frac{1}{v} - \frac{1}{v_0}\right)$$

(c) $P = \frac{u}{v}\cdot\frac{c+buv}{a+buv}$ and $T = \frac{u}{a+buv}$

$$\frac{1}{T} = \frac{a+buv}{u} = \frac{a}{u} + bv$$

$$\frac{P}{T} = \frac{c+buv}{v} = \frac{c}{v} + bu$$

$$\frac{\partial}{\partial v}\left(\frac{1}{T}\right)_u = b = \frac{\partial}{\partial u}\left(\frac{P}{T}\right)_v$$

$$ds = \frac{1}{T}du + \frac{P}{T}dv = \left(\frac{a}{u} + bv\right)du + \left(\frac{c}{v} + bu\right)dv$$

$$= d\left[a\ln u + c\ln v + buv\right]$$

$$\therefore \quad \underline{\underline{S = Ns_0 + Na\ln u + Nc\ln v + Nbuv}}$$

More systematic way of solving exact differential

$$\frac{\partial}{\partial u}F(u,v) = \frac{a}{u} + bv \rightarrow F(u,v) = a\ln u + buv + C(v)$$

$$\frac{\partial}{\partial v}F(u,v) = \frac{c}{v} + bu \qquad \frac{\partial F}{\partial v} = bu + C'(v) \qquad \therefore C'(v) = \frac{c}{v}$$

$$C(v) = c\ln v$$