

10.3 Given (10.3, 9): $(P + \frac{a}{v^2})(v-b) \approx kT$

(a) Solve for P, we get $P = \frac{kT}{v-b} - \frac{a}{v^2}$ (1)

The goal is to get $C_p - C_v$. We will assume N is constant. Then $C_v = \frac{\partial U}{\partial T}|_v$, $C_p = \frac{\partial U}{\partial T}|_p$
Let's get U.

By 10.7.8, $P = -\frac{\partial A}{\partial v}|_T = \frac{kT}{v-b} - \frac{a}{v^2} \Rightarrow -A = \int dv \left[\left(\frac{kT}{v-b} \right) - \frac{a}{v^2} \right]$

$\Rightarrow -A = kTN \ln(v-b) - \frac{aN^2}{v} + \mathcal{K}(T)$

where I have noted $v = \frac{V}{N}$, and carried out the integration. $\mathcal{K}(T)$ is a constant of integration, which may still have Temperature dependence.

By 3.3.5, $U = T^2 \left[\frac{\partial}{\partial T} \left(\frac{-A}{T} \right) \right]_v = -T^2 \frac{\partial}{\partial T} \left(\frac{Na}{vT} \right) + T^2 \frac{\partial}{\partial T} \left(\frac{\mathcal{K}(T)}{T} \right) = \frac{Na}{v} - \mathcal{K}'(T)$

Thus, we have $C_v = \frac{\partial U}{\partial T}|_v = -\mathcal{K}''(T) + Na \frac{\partial}{\partial T} \left(\frac{1}{v} \right)|_v = -\mathcal{K}''(T) + \frac{Na}{v^2} \frac{\partial v}{\partial T}|_v$

$C_p = \frac{\partial U}{\partial T}|_p = -\mathcal{K}''(T) - Na \frac{\partial}{\partial T} \left(\frac{1}{v} \right)|_p = -\mathcal{K}''(T) - \frac{Na}{v^2} \frac{\partial v}{\partial T}|_p$

$\Rightarrow C_p - C_v = -\frac{Na}{v^2} \frac{\partial v}{\partial T}|_p \stackrel{\text{By (1)}}{=} N \left(\frac{kT}{v-b} \right) \frac{\partial v}{\partial T}|_p - N P \frac{\partial v}{\partial T}|_p$ (2)

Now we find $\frac{\partial v}{\partial T}|_p$

Using (1), $\frac{\partial P}{\partial T}|_p = \frac{k}{v-b} + \left(\frac{2a}{v^3} - \frac{kT}{(v-b)^2} \right) \frac{\partial v}{\partial T}|_p \Rightarrow \frac{\partial v}{\partial T}|_p = \frac{k}{v-b} \left(\frac{1}{\frac{kT}{(v-b)^2} - \frac{2a}{v^3}} \right)$

Using (2) $\Rightarrow C_p - C_v = \frac{NkT}{v-b} \frac{k}{v-b} \left(\frac{kT}{(v-b)^2} - \frac{2a}{v^3} \right)^{-1} = \boxed{Nk \left(1 - \frac{2a(v-b)^2}{v^3 kT} \right)^{-1}}$ ✓

(b) By H.6b, $S = -\frac{\partial A}{\partial T}|_v$, and from part a, $-A = kTN \ln(v-b) - \frac{Na}{v} + \mathcal{K}(T)$

$\Rightarrow S = kN \ln(v-b) + \mathcal{K}'(T)$ (3)

We saw in part a that $U = \frac{Na}{v} - T^2 \frac{\partial}{\partial T} \left(\frac{\mathcal{K}(T)}{T} \right) = \frac{Na}{v} - T^2 \left(\frac{T\mathcal{K}'(T)}{T^2} - \frac{\mathcal{K}(T)}{T^2} \right)$

$\Rightarrow U = \frac{Na}{v} - \mathcal{K}'(T) \cdot T + \mathcal{K}(T)$

Again $C_v = \frac{\partial U}{\partial T}|_v = \cancel{\mathcal{K}'(T)} - \mathcal{K}''(T)T - \cancel{\mathcal{K}'(T)} = -\mathcal{K}''(T)T$

$\Rightarrow \frac{\partial^2 \mathcal{K}(T)}{\partial T^2} = -\frac{C_v}{T} \Rightarrow \frac{\partial \mathcal{K}(T)}{\partial T} = C_v \ln(T) + \text{constant}$

For adiabatic processes, $S = \text{constant}$. Using (3), and rolling the constants together,

$-kN \ln(v-b) = C_v \ln(T) + \text{const}$

$\Rightarrow \text{const} = kN \ln(v-b) + C_v \ln(T) = \ln[(v-b)^{Nk}] + \ln(T^{C_v})$

Other const. = $(v-b)^{Nk} T^{C_v} = [(v-b) T^{C_v/Nk}]^{Nk}$

$\boxed{(v-b) T^{C_v/Nk} = \text{constant}}$ ✓

10.3 ② Expanding into a vacuum requires no work or heating.
 $\Rightarrow U = \text{constant.}$

from ①: $U = \frac{Na}{\gamma} - \mathcal{R}(T) = \frac{Na}{\gamma} - C_V T + \text{constant.}$

Then we make 2 copies: $U_2 = \frac{N^2 a}{V_2} - C_V T_2$, $U_1 = \frac{N^2 a}{V_1} - C_V T_1$

$U_2 = U_1 \Rightarrow \frac{N^2 a}{V_2} - C_V T_2 = \frac{N^2 a}{V_1} - C_V T_1 \Rightarrow T_2 - T_1 = \frac{N^2 a}{C_V} \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$

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