Problem 6.3-2 Joule-Thomson process

Since the initial and final enthalpies are the same:

\[ U_i + P_i V_i = U_f + P_f V_f \]

We also know for this system that \( U = PV \)

Therefore:

\[ P_i V_i = P_f V_f \]

From the second equation of state:

\[ T = 3B \left( \frac{U^2}{NV} \right)^{1/3} = 3B \left( \frac{P^2V}{N} \right)^{1/3} \]

We derive:

\[ PV = \frac{N}{P} \left( \frac{T}{3B} \right)^3 \]

Therefore:

\[ \frac{N}{P_i} \left( \frac{T_i}{3B} \right)^3 = \frac{N}{P_f} \left( \frac{T_f}{3B} \right)^3 \quad \Rightarrow \quad \frac{T_i^3}{P_i} = \frac{T_f^3}{P_f} \quad \Rightarrow \quad T_f = T_i \left( \frac{P_f}{P_i} \right)^{1/3} \]
Problem 6.3 – 3 Joule-Thomson process for a vdW fluid

A) \[ P = \frac{RT}{v-b} - \frac{a}{v^2} \]
\[ \frac{1}{T} = \frac{cR}{u + a/v} \quad \Rightarrow \quad u = -\frac{a}{v} + cRT \]

\[ h = u + Pv = -\frac{a}{v} + cRT + \frac{vRT}{v-b} - \frac{a}{v} = -\frac{2a}{v} + RT \left( c + \frac{v}{v-b} \right) \]

\[ h_i = h_f \quad \Rightarrow \quad -\frac{2a}{v_i} + RT_i \left( c + \frac{v_i}{v_i-b} \right) = -\frac{2a}{v_f} + RT_f \left( c + \frac{v_f}{v_f-b} \right) \]

\[ T_f = \left( \frac{2a}{v_f} - \frac{2a}{v_i} + RT_i \left( c + \frac{v_i}{v_i-b} \right) \right) \bigg/ \left( Rc + \frac{Rv_f}{v_f-b} \right) \]

B) Estimating the small parameters of the expansion suggested by Callen for CO$_2$:
\[ P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \Rightarrow \quad v = 6.34 \times 10^{-5} \quad \Rightarrow \quad \varepsilon_1 = \frac{b}{v} = 0.67 \quad \varepsilon_2 = \frac{a}{RTv} = 2.8 \]

Small parameter expansion does not work, full numerical solution is required!
Problem 6.4–1 Chemical Reaction

a) The chemical reaction equation:

\[ H_2S + 2H_2O \Leftrightarrow SO_2 + 3H_2 \; \Rightarrow \; H_2S + 2H_2O - SO_2 - 3H_2 \Leftrightarrow 0 \]

Gives us the stoichiometric coefficients:

\[ v_{H_2S} = 1 \quad v_{H_2O} = 2 \quad v_{SO_2} = -1 \quad v_{H_2} = -3 \]

Therefore, the condition of chemical equilibrium:

\[ \sum_i v_i \mu_i = 0 \]

Becomes:

\[ \mu_{H_2S} + 2\mu_{H_2O} - \mu_{SO_2} - 3\mu_{H_2} = 0 \]
Problem 6.4–1 Chemical Reaction

b) Using the general expression for mole numbers in a chemical reaction:

\[ N_j = N_j^0 + v_j \Delta \tilde{N} \]

We can write mole numbers for each of the substances in the reaction:

\[ N_{H_2S} = \frac{1}{2} + \Delta \tilde{N} \]
\[ N_{H_2O} = \frac{3}{4} + 2\Delta \tilde{N} \quad \text{Vanishes at:} \quad \Delta \tilde{N} = \frac{3}{8} \]
\[ N_{SO_2} = 1 - \Delta \tilde{N} \]
\[ N_{H_2} = 2 - 3\Delta \tilde{N} \]
\[ \Delta \tilde{N} = \frac{1}{2} \]
\[ \Delta \tilde{N} = \frac{3}{8} \]
\[ \Delta \tilde{N} = 1 \]
\[ \Delta \tilde{N} = \frac{2}{3} \]
Problem 6.4–1 Chemical Reaction

c) For negative $\Delta \tilde{N}$ the first material that depletes is water at $\Delta \tilde{N}_{\text{min}} = -\frac{3}{8}$.

For positive $\Delta \tilde{N}$ the first material that depletes is hydrogen at $\Delta \tilde{N}_{\text{max}} = \frac{2}{3}$.

d) The degree of reaction is:

\[
\varepsilon = \frac{\Delta \tilde{N} - \Delta \tilde{N}_{\text{min}}}{\Delta \tilde{N}_{\text{max}} - \Delta \tilde{N}_{\text{min}}} \quad \varepsilon = \frac{1/4 + 3/8}{2/3 + 3/8} = \frac{3}{5}
\]

For $\Delta \tilde{N} = \frac{1}{4}$,

\[
N_{H_2S} = \frac{1}{2} + \Delta \tilde{N} = \frac{3}{4}
\]

\[
N_{H_2O} = \frac{3}{4} + 2\Delta \tilde{N} = \frac{5}{4}
\]

\[
N_{SO_2} = 1 - \Delta \tilde{N} = \frac{3}{4}
\]

\[
N_{H_2} = 2 - 3\Delta \tilde{N} = \frac{5}{4}
\]

\[
N_{\text{total}} = N_{H_2S} + N_{H_2O} + N_{SO_2} + N_{H_2} = 4
\]
**Problem 6.4–1 Chemical Reaction**

\[
x_{H_2S} = \frac{N_{H_2S}}{N_{total}} = \frac{3}{16}
\]

\[
x_{SO_2} = \frac{N_{SO_2}}{N_{total}} = \frac{3}{16}
\]

\[
x_{H_2O} = \frac{N_{H_2O}}{N_{total}} = \frac{5}{16}
\]

\[
x_{H_2} = \frac{N_{H_2}}{N_{total}} = \frac{5}{16}
\]

\[e) \text{ Since the nominal solution of the equilibrium condition give the value } \Delta \tilde{N} = 0.8\]

\[\text{exceeding the maximum value without depletion, } \Delta \tilde{N}_{\text{max}} = \frac{2}{3}\]

\[\text{the reaction will proceed to depletion and in equilibrium: } \Delta \tilde{N} = \Delta \tilde{N}_{\text{max}} = \frac{2}{3}\]

\[\varepsilon = \frac{\Delta \tilde{N} - \Delta \tilde{N}_{\text{min}}}{\Delta \tilde{N}_{\text{max}} - \Delta \tilde{N}_{\text{min}}} = 1\]

\[N_{H_2} = 0 \quad N_{SO_2} = \frac{1}{3} \quad N_{H_2O} = \frac{25}{12} \quad N_{H_2S} = \frac{7}{6}\]

\[N_{total} = \frac{43}{12}\]

\[x_{H_2} = 0 \quad x_{SO_2} = \frac{4}{43} \quad x_{H_2O} = \frac{25}{43} \quad x_{H_2S} = \frac{14}{43}\]
Problem 7.4 – 7 Maxwell Relations

\[ c_v = T \left( \frac{\partial s}{\partial T} \right)_v \quad \Rightarrow \quad \frac{\partial c_v}{\partial v} = T \frac{\partial^2 s}{\partial v \partial T} = T \frac{\partial^2 s}{\partial T \partial v} \]

Employing a Maxwell relation:

\[ \left( \frac{\partial s}{\partial v} \right)_T = \left( \frac{\partial P}{\partial T} \right)_v \]

We obtain:

\[ \left( \frac{\partial c_v}{\partial v} \right)_T = T \frac{\partial^2 s}{\partial T \partial v} = T \left( \frac{\partial^2 P}{\partial T^2} \right)_v \]

For a vdW fluid:

\[ P = \frac{RT}{v - b} - \frac{a}{v^2} \quad \Rightarrow \quad \left( \frac{\partial c_v}{\partial v} \right)_T = T \left( \frac{\partial^2 P}{\partial T^2} \right)_v = 0 \]
There are multiple ways of solving this problem.

We can write the Gibbs-Duhem relation:

$$d\mu = -sdT + vdP$$

Since $T$ and $\mu$ are constants, $dP$ is constant in any process, including the process of compression of the system. Therefore:

$$\frac{1}{V} \frac{dV}{dP} = \infty$$

The reason for diverging compressibility is permeability of the wall. There is no resistance to a piston changing the volume of the system.

Note that you cannot replace $\frac{1}{V} \frac{dV}{dP}$ with $\frac{1}{V} \left( \frac{dV}{dP} \right)_T$ as the latter is calculated at constant mole number, not constant chemical potential.
Given: \( P_0, T_0, v_0, P_f \)

\[ \kappa_T = \frac{A}{v^2} \quad \text{along OC isotherm} \]

\[ \alpha = \alpha_0 \quad \text{along OC isotherm} \]

\[ c_p = c_p^0 \quad \text{along CF isobar} \]

We know that the curve OF is isenthalp:

\[ H_0 = H_F \quad \Rightarrow \quad U_F - U_0 = P_0 V_0 - P_f V_f \quad (1) \]
Problem 7.4-24 Temperature in a Joule-Thomson process

\[ \kappa_T = -\frac{1}{v}\left( \frac{\partial v}{\partial P} \right)_T = \frac{A}{v^2} \quad \Rightarrow \quad \left( \frac{\partial v}{\partial P} \right)_T = -\frac{A}{v} \quad (2) \]

Since temperature does not change during the process OC, we can simply write:

\[ \frac{\partial v}{\partial P} = -\frac{A}{v} \quad \Rightarrow \quad vdv = -AdP \quad \Rightarrow \quad \frac{v^2 - v_0^2}{2} = -A\left( P - P_0 \right) \quad (3) \]

\[ P = P_0 + \frac{v_0^2 - v^2}{2A} \quad (3) \]

where \( P \) is pressure in a state on the OC line.

Equivalently:

\[ v^2 = v_0^2 + 2A\left( P_0 - P \right) \quad (4) \]

We also note that

\[ v_C^2 = v_0^2 - 2A\left( P_f - P_0 \right) \quad (5) \]
Problem 7.4-24 Temperature in a Joule-Thomson process

Let us now express work and heat transfer during processes OC and CF in terms of the given parameters of these processes.

\[ Q_{OC} = \int_{S_0}^{S_C} TdS = T_0 \int_{S_0}^{S_C} dS = T_0 (S_C - S_0) \]

\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \alpha_0 \]

By a Maxwell relation:

\[ \left( \frac{\partial S}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P \quad \implies \quad \left( \frac{\partial S}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P = -V\alpha_0 \]

Since OC process is at constant temperature, we can write:

\[ dS = -V\alpha_0 dP \quad \implies \quad S_C - S_O = -\alpha_0 \int_{P_0}^{P_f} VdP \]
Problem 7.4-24 Temperature in a Joule-Thomson process

Using equation (4):

\[ S_C - S_O = -\alpha_0 \int_{P_o}^{P_f} VdP = -\alpha_0 N \int_{P_o}^{P_f} \sqrt{v_0^2 + 2A(P_0 - P)}dP \]

\[ S_C - S_O = \frac{\alpha_0 N}{3A} \left( v_0^2 + 2A(P_0 - P) \right)^{3/2} \bigg|_{P_o}^{P_f} = -\frac{\alpha_0 N}{3A} \left( v_0^3 - \left( v_0^2 + 2A(P_0 - P_f) \right)^{3/2} \right) \]

\[ Q_{OC} = -\frac{\alpha_0 NT_0}{3A} \left( v_0^3 - \left( v_0^2 + 2A(P_0 - P_f) \right)^{3/2} \right) \quad (6) \]

\[ W_{OC}: \quad W_{OC} = -\int_{v_0}^{v_C} PdV \quad \text{Using equation (3)}: \]

\[ W_{OC} = -\int_{v_0}^{v_C} PdV = -N \int_{v_0}^{v_C} \left( P_0 + \frac{v_0^2 - v^2}{2A} \right) dv = -N\left( P_0 + \frac{v_0^2}{2A} \right)(v_C - v_0) + \frac{N}{6A} \left( v_C^3 - v_0^3 \right) \quad (7) \]
Problem 7.4-24 Temperature in a Joule-Thomson process

Q\(_{\text{CF}}\):  
\[ Nc_P = \left( \frac{\partial Q}{\partial T} \right)_P = Nc_P^0 \]

Since pressure does not change during the process CF, we can write:

\[ Q_{\text{CF}} = Nc_P^0 \left( T_f - T_0 \right) \quad (8) \]

W\(_{\text{CF}}\):

\[ W_{\text{CF}} = - \int_{v_C}^{v_F} P \, dV = -P_f \int_{v_C}^{v_F} dV = -P_f \left( V_f - V_C \right) \quad (9) \]

From the conservation of energy:

\[ U_C - U_O = W_{\text{OC}} + Q_{\text{OC}} = \]

\[ - N \left( P_0 + \frac{v_0^2}{2A} \right) \left( v_C - v_0 \right) + \frac{N}{6A} \left( v_C^3 - v_0^3 \right) - \frac{\alpha_0 N T_0}{3A} \left( v_0^3 - \left( v_0^2 + 2A \left( P_0 - P_f \right) \right)^{3/2} \right) \]
Problem 7.4-24 Temperature in a Joule-Thomson process

\[ U_F - U_C = W_{CF} + Q_{CF} = -P_f (V_f - V_C) + Nc_P^0 (T_f - T_0) \]

\[ U_F - U_O = (U_F - U_C) + (U_C - U_O) = -NP_f (V_f - V_C) + Nc_P^0 (T_f - T_0) - \]

\[ N \left( P_0 + \frac{v_0^2}{2A} \right) (v_C - v_0) + \frac{N}{6A} (v_C^3 - v_0^3) - \frac{\alpha_0 N T_0}{3A} \left( v_0^3 - \left( v_0^2 + 2A(P_0 - P_f) \right)^{3/2} \right) \]

Using equation (1):

\[ P_0 v_0 - P_f v_f = -P_f (V_f - V_C) + c_P^0 (T_f - T_0) - \]

\[ \left( P_0 + \frac{v_0^2}{2A} \right) (v_C - v_0) + \frac{1}{6A} (v_C^3 - v_0^3) - \frac{\alpha_0 T_0}{3A} \left( v_0^3 - \left( v_0^2 + 2A(P_0 - P_f) \right)^{3/2} \right) \]  \hspace{1cm} (10)

Where according to equation (5):

\[ v_C = \sqrt{v_0^2 - 2A(P_f - P_0)} \]
**Problem 7.4-24 Temperature in a Joule-Thomson process**

Solving equation (10) for $T_f$ (note that the terms with $v_f$ cancel):

$$T_f = T_0 + \frac{P_0 v_0 - P_f v_C}{c_p^0} + \left( P_0 + \frac{v_0^2}{2A} \right) \left( v_C - v_0 \right) - \frac{\left( v_C^3 - v_0^3 \right)}{6A c_p^0} + \frac{\alpha_0 T_0}{3A c_p^0} \left( v_0^3 - \left( v_0^2 + 2A(P_0 - P_f) \right)^{3/2} \right)$$

where $v_C = \sqrt{v_0^2 - 2A(P_f - P_0)}$

After some algebra the above expression simplifies to:

$$T_f = T_0 - \frac{(1 - \alpha_0 T_0)}{3A c_p^0} \left( v_0^3 - \left( v_0^2 + 2A(P_0 - P_f) \right)^{3/2} \right)$$

The condition for temperature being lowered in this process is:

$$1 - \alpha_0 T_0 < 0 \quad \quad \quad \alpha_0 > 0 \quad \quad \quad T_0 > \left( \frac{1}{\alpha_0} \right)$$

(compare to equations 6.41 and 6.42)
Expressing $P$ and $T$ in terms of $h$ and $v$:

$$P = \frac{(h + 2a/v)}{c(v - b) + v} - \frac{a}{v^2}; T = \frac{h + 2a/v}{R(c + v/(v - b))}$$

and using a parametric plot with $v$ as a parameter:

The fact that isenthalpic curves intersect at small values of molar enthalpy (and low $T$) tells us that for some values of $P$ and $T$ there exist two states with different values of molar enthalpy $h$. You can check that these states differ by molar volumes. The existence of two states with different molar volumes at the same $T$ and $P$ values signals a first order phase transition (condensation).

Helium needs to be pre-cooled in order for Joule-Thomson process to cool the gas because the inversion temperature of He is quite low ~ 35 K. Note that pre-cooling to the liquid nitrogen temperature (77 K) is not enough to make the Joule-Thomson process efficient. This is why liquid helium is difficult to liquefy and this is mainly why it costs ~ 5$ per liter, one order of magnitude more expensive than liquid nitrogen.