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

We derive: $$PV = \frac{N}{P}\left(\frac{T}{3B}\right)^3$$

Therefore: $$\frac{N}{P_i}\left(\frac{T_i}{3B}\right)^3 = \frac{N}{P_f}\left(\frac{T_f}{3B}\right)^3 \Rightarrow \frac{T_i^3}{P_i} = \frac{T_f^3}{P_f} \Rightarrow T_f = T_i\left(\frac{P_f}{P_i}\right)^{1/3}$$

Problem 6.3 – 3 Joule-Thomson process for a vdW fluid

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

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

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

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

B) Estimating the small parameters of the expansion suggested by Callen for CO_2:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \Rightarrow \quad v = 6.34\times10^{-5} \quad \Rightarrow \quad \varepsilon_1 = \frac{b}{v} = 0.67 \quad \varepsilon_2 = \frac{a}{RTv} = 2.8$$

Small parameter expansion does not work, full numerical solution is required!

Problem 6.4–1 Chemical Reaction

a) The chemical reaction equation:

$$H_2S + 2H_2O \Leftrightarrow SO_2 + 3H_2 \quad \Longrightarrow \quad H_2S + 2H_2O - SO_2 - 3H_2 \Leftrightarrow 0$$

Gives us the stoichiometric coefficients:

$$v_{H_2S} = 1 \qquad v_{H_2O} = 2 \qquad v_{SO_2} = -1 \qquad v_{H_2} = -3$$

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:

$$N_{H_2S} = \frac{1}{2} + \Delta\tilde{N}$$

$$N_{H_2O} = \frac{3}{4} + 2\Delta\tilde{N}$$

$$N_{SO_2} = 1 - \Delta\tilde{N}$$

$$N_{H_2} = 2 - 3\Delta\tilde{N}$$

Vanishes at:

$$\Delta\tilde{N} = -\frac{1}{2}$$

$$\Delta\tilde{N} = -\frac{3}{8}$$

$$\Delta\tilde{N} = 1$$

$$\Delta\tilde{N} = \frac{2}{3}$$

Problem 6.4–1 Chemical Reaction

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

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

d) The degree of reaction is:

$$\varepsilon = \frac{\Delta\tilde{N} - \Delta\tilde{N}_{\min}}{\Delta\tilde{N}_{\max} - \Delta\tilde{N}_{\min}}$$

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

$$\varepsilon = \frac{1/4 + 3/8}{2/3 + 3/8} = \frac{3}{5}$$

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

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

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

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

$$N_{total} = N_{H_2S} + N_{H_2O} + N_{SO_2} + N_{H_2} = 4$$

Problem 6.4–1 Chemical Reaction

$$x_{H_2S} = \frac{N_{H_2S}}{N_{total}} = \frac{3}{16} \qquad x_{SO_2} = \frac{N_{SO_2}}{N_{total}} = \frac{3}{16}$$

$$x_{H_2O} = \frac{N_{H_2O}}{N_{total}} = \frac{5}{16} \qquad x_{H_2} = \frac{N_{H_2}}{N_{total}} = \frac{5}{16}$$

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

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

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

$$\varepsilon = \frac{\Delta\tilde{N} - \Delta\tilde{N}_{\min}}{\Delta\tilde{N}_{\max} - \Delta\tilde{N}_{\min}} = 1 \qquad N_{H_2} = 0 \quad N_{SO_2} = \frac{1}{3} \quad N_{H_2O} = \frac{25}{12} \quad N_{H_2S} = \frac{7}{6}$$

$$N_{total} = \frac{43}{12} \qquad x_{H_2} = 0 \quad x_{SO_2} = \frac{4}{43} \quad x_{H_2O} = \frac{25}{43} \quad x_{H_2S} = \frac{14}{43}$$

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:

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0$$

Problem 7.4 – 18 Compressibility

There are multiple ways of solving this problem.

We can write the Gibbs-Duhem relation:

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

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

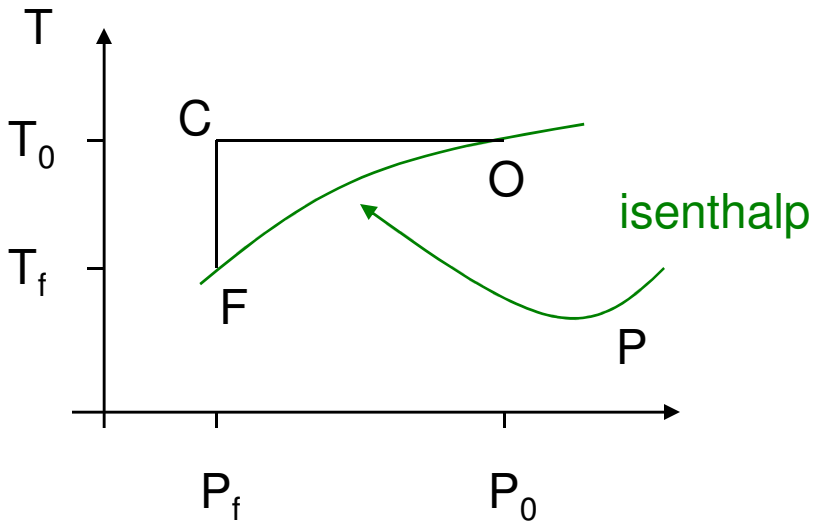
$$\frac{1}{V}\frac{dV}{dP} = \infty$$

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.

Problem 7.4-24 Temperature in a Joule-Thomson process



Given: $P_0,\ T_0,\ v_0,\ P_f$

$$\kappa_T = \frac{A}{v^2}$$ along OC isotherm

$$\alpha = \alpha_0$$ along OC isotherm

$$c_P = c_P^0$$ along CF isobar

We know that the curve OF is isenthalp:

$$H_0 = H_F \quad \Rightarrow \quad U_F - U_0 = P_0 V_0 - P_f V_f \qquad (1)$$

Problem 7.4-24 Temperature in a Joule-Thomson process

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

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

$$\frac{\partial v}{\partial P} = -\frac{A}{v} \Rightarrow v dv = -A dP \Rightarrow \frac{v^2 - v_0^2}{2} = -A\left(P - P_0\right) \Rightarrow$$

$$P = P_0 + \frac{v_0^2 - v^2}{2A} \qquad (3)$$ where P is pressure in a state on the OC line.

Equivalently:

$$v^2 = v_0^2 + 2A\left(P_0 - P\right) \qquad (4)$$

We also note that $$v_C^2 = v_0^2 - 2A\left(P_f - P_0\right) \qquad (5)$$

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}:
$$Q_{OC} = \int_{S_0}^{S_C} T dS = T_0 \int_{S_0}^{S_C} dS = T_0 \left(S_C - S_0 \right)$$

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

By a Maxwell relation:
$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha_0$$

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

$$dS = -V\alpha_0 dP \Rightarrow \quad S_C - S_O = -\alpha_0 \int_{P_O}^{P_f} V dP$$

Problem 7.4-24 Temperature in a Joule-Thomson process

Using equation (4): $$S_C - S_O = -\alpha_0 \int_{P_O}^{P_f} V dP = -\alpha_0 N \int_{P_O}^{P_f} \sqrt{v_0^2 + 2A(P_0 - P)}\, dP$$

$$S_C - S_O = \frac{\alpha_0 N}{3A}\left(v_0^2 + 2A(P_0 - P)\right)^{3/2}\Big|_{P_O}^{P_f} = -\frac{\alpha_0 N}{3A}\left(v_0^3 - \left(v_0^2 + 2A(P_0 - P_f)\right)^{3/2}\right)$$

$$Q_{OC} = -\frac{\alpha_0 N T_0}{3A}\left(v_0^3 - \left(v_0^2 + 2A(P_0 - P_f)\right)^{3/2}\right) \qquad (6)$$

W_{OC}: $$W_{OC} = -\int_{V_0}^{V_C} P dV$$ Using equation (3):

$$W_{OC} = -\int_{V_0}^{V_C} P dV = -N \int_{v_0}^{v_C} \left(P_0 + \frac{v_0^2 - v^2}{2A}\right) dv = -N\left(P_0 + \frac{v_0^2}{2A}\right)(v_C - v_0) + \frac{N}{6A}\left(v_C^3 - v_0^3\right)$$

(7)

Problem 7.4-24 Temperature in a Joule-Thomson process

Q_{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:

$$Q_{CF} = Nc_P^0\left(T_f - T_0\right) \qquad (8)$$

W_{CF}:

$$W_{CF} = -\int_{V_C}^{V_F} P dV = -P_f \int_{V_C}^{V_F} dV = -P_f\left(V_f - V_C\right) \qquad (9)$$

From the conservation of energy:

$$U_C - U_O = W_{OC} + Q_{OC} =$$

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

Problem 7.4-24 Temperature in a Joule-Thomson process

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

$$U_F - U_O = \left(U_F - U_C\right) + \left(U_C - U_O\right) = -NP_f\left(v_f - v_C\right) + Nc_P^0\left(T_f - T_0\right) -$$

$$N\left(P_0 + \frac{v_0^2}{2A}\right)\left(v_C - v_0\right) + \frac{N}{6A}\left(v_C^3 - v_0^3\right) - \frac{\alpha_0 NT_0}{3A}\left(v_0^3 - \left(v_0^2 + 2A\left(P_0 - P_f\right)\right)^{3/2}\right)$$

Using equation (1):

$$P_0 v_0 - P_f v_f = -P_f\left(v_f - v_C\right) + c_P^0\left(T_f - T_0\right) -$$

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

Where according to equation (5): $v_C = \sqrt{v_0^2 - 2A\left(P_f - P_0\right)}$

Problem 7.4-24 Temperature in a Joule-Thomson process

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

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

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

After some algebra the above expression simplifies to:

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

The condition for temperature being lowered in this process is:

$$1 - \alpha_0 T_0 < 0 \quad \Rightarrow \quad \alpha_0 > 0 \quad \boxed{T_0 > \frac{1}{\alpha_0}}$$

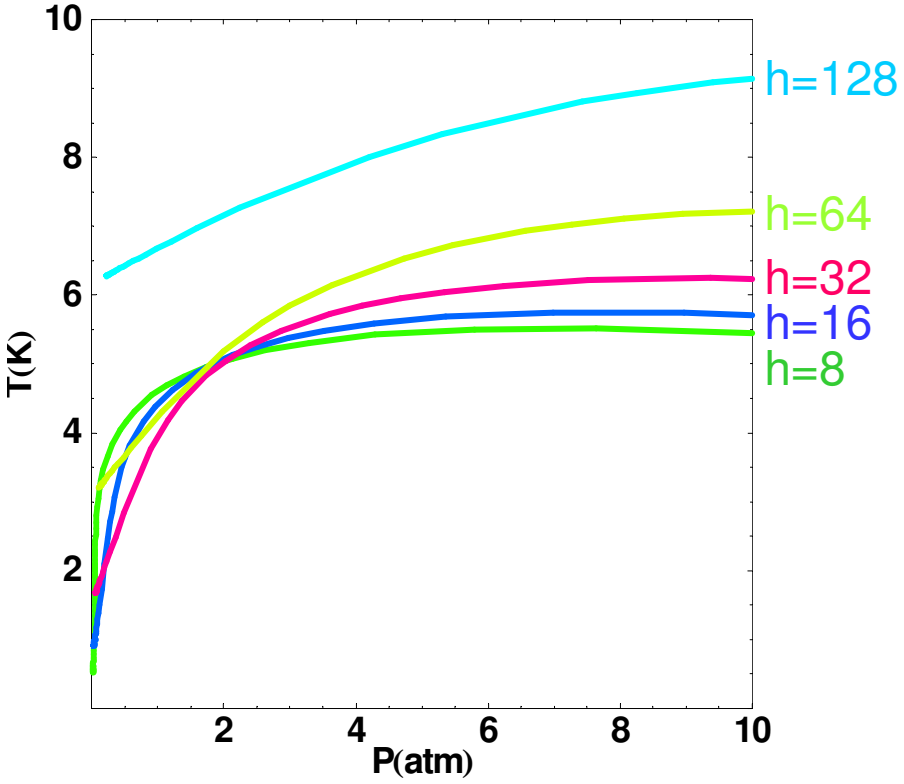
(compare to equations 6.41 and 6.42)

Isenthalpic curves of He

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.