

Homework 5: Problem 5.33

March 17, 2008

Use the van der Waals equation of state to plot the inversion line for N_2 on a PT diagram.

The inversion line is the line on a PT diagram which separates the positive and negative Joule-Thompson coefficients. Thus, we are asked to find the temperature and pressure at which $\mu_{JT} = 0$. From Equation 5.75 on page 239 in the text, we know that:

$$\begin{aligned}\mu_{JT} &= \left(\frac{\partial T}{\partial P} \right)_h \\ &= \frac{T \left(\frac{\partial v}{\partial T} \right)_p - v}{c_p} \\ &= 0\end{aligned}$$

We don't need to calculate the heat capacity. Since the heat capacity is always positive, and since we're setting $\mu_{JT} = 0$, we must solve for the temperature and specific volume such that:

$$0 = T \left(\frac{\partial v}{\partial T} \right)_p - v \quad (1)$$

[+2 points]

We can evaluate the partial derivative in Equation (1) as written, despite being given a pressure-explicit equation of state. Alternatively, we can save ourselves some calculus and make use of some of the handy rules for partial derivatives.

$$\begin{aligned}
P &= \frac{RT}{v-b} - \frac{a}{v^2} \\
\left(\frac{\partial P}{\partial T}\right)_v &= \frac{R}{(v-b)} \\
\left(\frac{\partial P}{\partial v}\right)_T &= -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}
\end{aligned}$$

From which it follows that:

$$\begin{aligned}
T \left(\frac{\partial v}{\partial T}\right)_P &= -T \frac{\left(\frac{\partial P}{\partial T}\right)_v}{\left(\frac{\partial P}{\partial v}\right)_T} \\
&= -\frac{RT/(v-b)}{-\frac{RT}{(v-b)^2} + \frac{2a}{v^3}}
\end{aligned}$$

Plugging this result into Equation (1) yields:

$$0 = \frac{RT}{(v-b) \left(\frac{RT}{(v-b)^2} - \frac{2a}{v^3}\right)} - v$$

which can be solved for temperature as a function of molar volume:

$$T_{JT} = \frac{2a(v_{JT} - b)^2}{Rv_{JT}^2 b} \quad (2)$$

[+3 points]

Similarly, we can use the equation of state to solve for the pressure:

$$P_{JT} = \frac{RT_{JT}}{v_{JT} - b} - \frac{a}{v_{JT}^2} \quad (3)$$

Next, use the critical data for nitrogen to obtain the van der Waals parameters:

$$\begin{aligned}T_c &= 126.2 \text{ [K]} \\P_c &= 33.84 \text{ [bar]}\end{aligned}$$

$$\begin{aligned}a &= \frac{27}{64} \frac{(RT_c)^2}{P_c} \\&= 1.373 \times 10^{-6} \text{ [bar m}^6 \text{ / mole}^2\text{]}\end{aligned}$$

$$\begin{aligned}b &= \frac{RT_c}{8P_c} \\&= 3.876 \times 10^{-5} \text{ [m}^3 \text{ / mole]}\end{aligned}$$

Since both T and P are explicit functions of v_{JT} , we must begin with an initial array for the specific volume. We know that $v_{JT} > b$ for the pressure to be positive. After some algebraic manipulation, we find that $P_{JT} = 0$ when $v_{JT} = 3/2b$ is substituted into Equations (2) and (3). Thus, we begin with $v_{JT} \in [3/2b, 1000b]$. Substituting this array into Equations (2) and (3) and plotting the results yields:

