

PHYS 461: Homework # 3

3.1 In terms of the variables T and P , the element of enthalpy dH is given by

$$dH = T dS + V dP = C_P dT + (h + V) dP,$$

where the calorimetric coefficient h is given by

$$h = -T \left(\frac{\partial V}{\partial T} \right)_P = -TV\alpha.$$

The expression of the Joule-Thomson coefficient is therefore

$$\mu_{JT} = \frac{V(\alpha T - 1)}{C_P}.$$

Since, for an ideal gas,

$$\alpha = \frac{1}{T} \quad \text{then} \quad \mu_{JT} = 0.$$

The equation of state of a mole of van der Waals gas can be written

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

Hence,

$$dP = \frac{R}{V - b} dT - \frac{RT}{(V - b)^2} dV + \frac{2a}{V^3} dV.$$

The expression of the coefficient of thermal expansion of a van der Waals gas is therefore given by

$$\begin{aligned} \alpha &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \\ &= \frac{V - b}{VT - \frac{2a}{R} \left(\frac{V - b}{V} \right)^2}, \end{aligned}$$

and the expression of the Joule-Thomson coefficient of a van der Waals gas is

$$\mu_{JT} = \frac{\frac{2a}{RT} \left(\frac{V-b}{V}\right)^2 - b}{C_P \left(1 - \frac{2a}{RVT} \left(\frac{V-b}{V}\right)^2\right)}.$$

If we assume that b/V is small and that we can neglect $(b/V)^2$, then

$$\left(\frac{V-b}{V}\right)^2 \approx \left(1 - \frac{2b}{V}\right).$$

To first order in b/V , the condition $\mu_{JT} = 0$ is

$$\frac{2a}{RT} \left(1 - \frac{2b}{V}\right) = b.$$

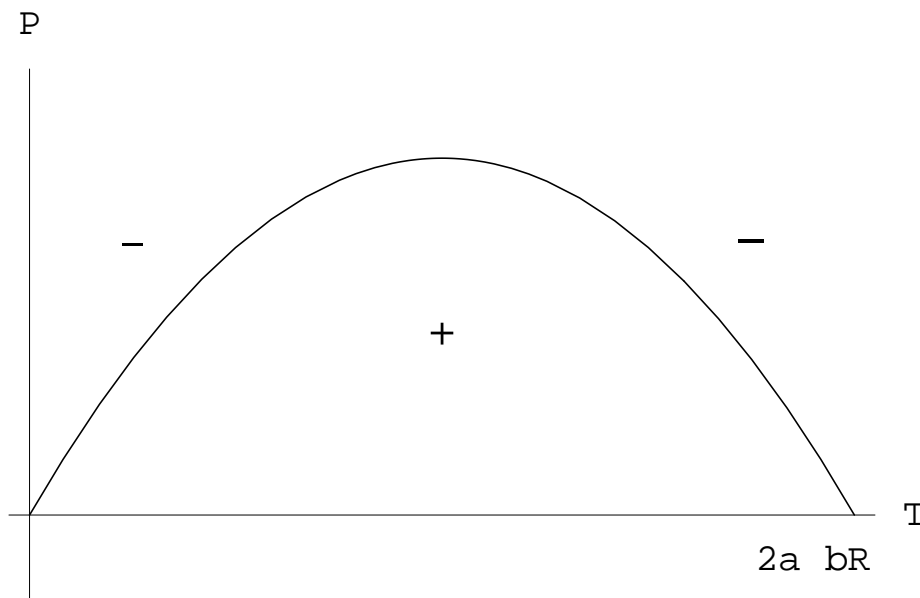
To express the condition $\mu_{JT} = 0$ in terms of the variables T and P , we have to use the van der Waals equation of state to replace V by its expression in terms of T and P .

Since V appear in a small term (first order in b/V) we can just replace V by RT/P (order zero term). This yields

$$4abP = 2aRT - bR^2T^2.$$

In the (T, P) -plane, this is the equation of a parabola. We verify that in the domain of the (T, P) -plane limited by the parabola and the T -axis the coefficient $\mu_{JT} > 0$, while outside of this domain $\mu_{JT} < 0$.

Figure Graph in the (T, P) -plane of $\mu_{JT}(T, P) = 0$.



3.2 From the relation

$$-\left(\frac{\partial \log P}{\partial \log V}\right)_S = \frac{C_P}{C_V},$$

it follows that

$$-\frac{V}{P} \left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{P\chi_S} = \frac{C_P}{C_V}.$$

Since

$$\frac{\chi_T}{\chi_S} = \frac{C_P}{C_V},$$

we find

$$\chi_T = \frac{1}{P}.$$

Hence,

$$-\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{P}.$$

At constant T , this last relation implies

$$\frac{dV}{V} + \frac{dP}{P} = \text{constant},$$

which shows that PV is a function of T only.

3.3 We have

$$\begin{aligned}\frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial T}\right)_S} &= \frac{\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}}{\frac{(\partial S/\partial T)_P}{(\partial S/\partial P)_T}} \\ &= \frac{-\left(\frac{\partial V}{\partial T}\right)_P^2}{-\frac{V\chi_T C_P}{T}} \\ &= \frac{VT\alpha^2}{\chi_T C_P} \\ &= \frac{C_P - C_V}{C_V}.\end{aligned}$$