

Joule-Thomson Coefficient for Ideal Gas

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_p \mu_{JT} \quad \text{where } \mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

Go back to 5.75

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_T - V = -T \left(\frac{\partial V}{\partial T}\right)_P}$$

Thus

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V$$

For Ideal Gas

$$V = \frac{nRT}{P} \rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

Substitute

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{nR}{P}\right) + V = -V + V = 0$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] \left(\frac{\partial V}{\partial P}\right)_T + V$$

use 5.61

$$P + \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V \quad \text{Thus}$$

$$T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T + V$$

$$P = \frac{nRT}{V}; \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \quad V = \frac{nRT}{P} \Rightarrow \frac{nRT}{P^2} = \left(\frac{\partial V}{\partial P}\right)_T$$

Substitute

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{nR}{V}\right) \left(-\frac{nRT}{P^2}\right) + V = T \cdot P \cdot \left(-\frac{V}{P}\right) = -V + V = 0$$

The van der Waals gas and the Joule Thompson Coefficient

We begin with the connection between the JT Coefficient and any gas:

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_p \mu_{JT} = V - T \left(\frac{\partial V}{\partial T}\right)_P$$

or

$$I = \left(\frac{\partial H_m}{\partial P}\right)_T = -C_{p,m} \mu_{JT} = V_m - T \left(\frac{\partial V_m}{\partial T}\right)_P$$

The I is just a shorthand for the partial derivative of the enthalpy. From here we use the vdW gas equation of state to evaluate this derivative:

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

The easier route seems to be to evaluate $\left(\frac{\partial T}{\partial V_m}\right)_P$. Taking the derivatives:

$$0 = \frac{R}{(V_m - b)} \left(\frac{\partial T}{\partial V_m}\right)_P - \frac{RT}{(V_m - b)^2} + 2 \frac{a}{V_m^3}$$

Rearrange this equation to solve for the derivative and take the reciprocal:

$$I = V_m - T \left(\frac{\partial V_m}{\partial T}\right)_P = V_m - \frac{\frac{RT}{(V_m - b)}}{\frac{RT}{(V_m - b)^2} - 2 \frac{a}{V_m^3}} = V_m - \frac{(V_m - b)}{1 - 2 \frac{a(V_m - b)^2}{RTV_m^3}}$$

This is the quantity of interest which is proportional to the JT coefficient. As a quick check, if $a=0$ then $I=b$. This is consistent with 3.54 in the text. This is a complete description of the JT coefficient for the vdW gas. We can rearrange it a bit more to simplify and cancel some of the terms:

Let $\zeta = \left\{ 2 \frac{a(V_m - b)^2}{RTV_m^3} \right\}$. Then the coefficient is given by:

$$I = -C_{p,m} \mu_{JT} = V_m - \frac{(V_m - b)}{1 - \zeta} = b - (V_m - b) \frac{\zeta}{1 - \zeta}$$

Notice that $\zeta(V_m - b) = \left\{ \frac{2a}{KT} \left(\frac{V_m - b}{V_m} \right)^3 \right\}$. So this term is well behaved for any

molar volume. In the limit as V_m goes to infinity (or the density of the gas goes to zero) the gas should behave as an ideal gas. But if we are careful now we can take this form to its limiting value and have a non zero JT coefficient even when the gas is behaving as an ideal gas.

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$$\lim_{P \rightarrow \infty} \left\{ \zeta(V_m - b) \right\} = \frac{2a}{RT} \text{ and } \lim_{P \rightarrow \infty} \{\zeta\} = 0. \text{ These limits give equation 3.54.}$$

$$I = -C_{p,m} \mu_{JT} = V_m - \frac{(V_m - b)}{1 - \zeta} = \lim_{P \rightarrow \infty} \left\{ b - (V_m - b) \frac{\zeta}{1 - \zeta} \right\} = b - \frac{2a}{RT}$$

In terms of figure 3.6 (where temperature is plotted as a function of pressure) we would have a straight line at a fixed temperature. And the JT coefficient would be positive at low temperature and negative at high temperatures, and be independent of the pressure. The point where the JTC would vanish is:

$$0 = b - \frac{2a}{RT_{JT}}$$

$$RT_{JT} = \frac{2a}{b}$$

This should be the limiting value in Figure 3.6 when the pressure goes to zero.

Now let's solve the more complete equation for all pressures. This can be done by finding the set of points (i.e. the line) when the JTC vanishes. Therefore we seek the set of points were:

$$0 = b - (V_m - b) \frac{\zeta}{1 - \zeta}$$

$$\frac{\zeta}{1 - \zeta} = \frac{b}{(V_m - b)}$$

$$\zeta = \frac{b}{V_m}$$

The strategy then is to choose a set of molar volumes $0 < (V_m - b) < \infty$. From there we can solve for the Temperature at which the JTC vanishes:

$$\frac{b}{V_m} = \left\{ 2 \frac{a(V_m - b)^2}{RT_{JT}V_m^3} \right\}$$

$$RT_{JT} = \frac{2a}{b} \cdot \left(\frac{V_m - b}{V_m} \right)^2$$

Notice now that when V_m goes to infinity (eqn 3.54) is recovered. Now that we have the volume and the temperature, we can compute the pressure at which the JTC for the gas is zero.