Relating the Joule-Thompson Coefficient to the Van der Waals Constants

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The definition for the Joule-Thompson Coefficient is given in equation 1 below

$$\mu \equiv -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} \tag{1}$$

In order to relate the Joule-Thompson Coefficient to the Van der Waals Constants, we must first take a closer look at enthalpy (H). Enthalpy is defined as $H = U + PV$, and is a function of multiple variables. Therefore, we can express its exact differential in multiple ways. We may not have completely covered this yet in lecture, but essentially H is a 2-dimensional function and we can take the partial derivatives with respect to different pairs of variables. For thermodynamic potentials, one pair of variables is called the "Natural Variables" because their partial derivatives *are themselves* state variables. For enthalpy, the natural variables are S and P, and the exact differential is given below

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \tag{2}$$

Since $\left(\frac{\partial H}{\partial S}\right)_P = T$ and $\left(\frac{\partial H}{\partial P}\right)_S = V$, the expression simplifies to the expression below. This is the neat result of using the *natural variables*:

$$dH = TdS + VdP \tag{3}$$

However, for U and H it is useful to take derivatives with respect to temperature as well, even though it is not a natural variable for those potentials.

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For enthalpy the exact derivative is given below:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{4}$$

And $\left(\frac{\partial H}{\partial T}\right)_P$ is the constant-pressure heat capacity c_P. We can't simplify the other part yet, but so far this gives us:

$$dH = c_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{5}$$

Now we can return to equation 3, and differential with respect to P at constant temperature. In practice, this means that we change all our ds into ∂s, put ∂P in the denominator on both sides, and now hold T constant. The ∂P in the final term will cancel. The result is:

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \tag{6}$$

Now we can plug this into the other exact differential equation for H, equation 5 to get:

$$dH = c_P dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right]_T dP \tag{7}$$

Here we have a partial derivative of one state variable with respect to another state variable. This is an ideal time to consider using a Maxwell relation, which we also haven't covered. Wikipedia has two pages that are useful references for thermodynamic potentials and Maxwells relations.

- https://en.wikipedia.org/wiki/Thermodynamic_potential

- https://en.wikipedia.org/wiki/Maxwell_relations

In this instance, we specifically need the Maxwell relation: $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$. Using this relation gives us:

$$dH = c_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]_T dP \tag{8}$$

And remember that $\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]_T = \left(\frac{\partial H}{\partial P}\right)_T$, so we can revisit our original definition of the Joule-Thompson coefficient in equation 1:

$$\mu \equiv -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]_T}{c_P} = \frac{\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]_T}{c_P} \tag{9}$$