

1.5: Corresponding States

The fact that the critical point is unique for each gas provides a way to create a real gas law that applies to all gases. To do so, we first define what are called reduced units, which are $P^* = \frac{P}{P_c}$, $T^* = \frac{T}{T_c}$, and $V^* = \frac{V_m}{V_{c,m}}$, where P_c , T_c , and $V_{c,m}$ are the critical pressure, temperature, and per molar volume, respectively. Note that we can cleverly determine pressure from the reduced pressure via: $P = P^* \cdot P_c$ and likewise for temperature and per molar volume. Now take the van der Waals equation where we absorb n into V (the per molar form): $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$ and insert P , V_m , and T as in the above example:


$$P^* \cdot P_c = \frac{R \cdot T^* \cdot T_c}{V^* \cdot V_{c,m} - b} - \frac{a}{(V^* \cdot V_{c,m})^2}$$

Now the trick is that we know what the critical values of pressure, temperature and volume are from our previous discussion. Plug these into the above and we find:

$$P^* \frac{a}{27b^2} = \frac{R \cdot T^* \frac{8a}{27Rb}}{V^* \cdot 3b - b} - \frac{a}{V^{*2} \cdot 9b^2}$$

While painful, the use of middle school algebra yields the following: $P^* = \frac{T^* 8ab}{a \cdot (V^* \cdot 3b - b)} - \frac{27b^2 a}{a \cdot V^{*2} \cdot 9b^2}$ which is further reduced into:

$$P^* = \frac{8T^*}{3V^* - 1} - \frac{3}{V^{*2}} \quad (1.5.1)$$

 You are probably thinking- so what? There is a subtle property of the reduced form of the van der Waals equation of state- there are no a or b coefficients! And since these are unique to every gas, the reduced van der Waals equation applies to *every* gas.

To demonstrate how this is true, plotted in Figure 1.6 are the compression factors for 10 gases as a function of their reduced pressures and temperatures. Clearly the data cluster along similar isothermal lines, which reveals that they have fundamentally similar interactions as revealed by reduced real gas equations of state. However, as in the case of predicting the compression factor of helium gas shown in Figure 1.3, the van der Waals does not accurately reproduce the data shown in Figure 1.6. Instead, we have used the Redlich-Kwong equation of state:

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} \cdot V_m (V_m + b)} \quad (1.5.2)$$

which differs from the van der Waals in how the attractive forces are minimized by the $\frac{1}{\sqrt{T}}$ temperature factor in the “ a ” term. This has been shown to substantially increase the accuracy of the equation in the supercritical regions of the phase diagram. Last, there are a multitude of other, even more complex equations of state incorporating even more empirical constants and higher order terms. One should realize that, mathematically, it is impossible to not realize greater accuracy using longer equations with more parameters. If this is one’s end goal, then great; however, it is questionable whether one gains physical insight into the underlying mechanisms of molecular-molecular interactions, which is the goal of Physical Chemistry.

Conclusion. We have shown here that the perfect gas law isn’t all that perfect. Deviations from such a simple equation are expected based on the identity of the molecules that make the gas. The van der Waals and Virial equations account for much of this behavior, which can be understood by the fundamental properties of the molecules that comprise the gas. Specifically, that molecules are generally attracted to each other, but if they get too close then collisions occur! As will be demonstrated in later chapters, these real gas behaviors modify thermodynamic processes, and are responsible for some important applications such as refrigeration.

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