

## 1.3: The Virial Equation

Speaking of the inaccuracies of the van der Waals equation, when applied to the compression factors for helium shown in Figure 1.3C the van der Waals equation is substantially in error. Now engineers, who must make sure things like boilers and nuclear reactors don't explode, must have very accurate equations of state and thus sometimes the van der Waals relation doesn't cut it. In this regard, one way to accurately fit data is to use a series expansion. For example, let's rewrite the compression factor for the perfect gas law as:  $\frac{PV}{nRT} = 1$ , but now expand the right side of the equation in a power series of the molar density  $\frac{n}{V}$ :

$$\frac{PV}{nRT} = 1.0 + B(T) \cdot \left(\frac{n}{V}\right) + C(T) \left(\frac{n}{V}\right)^2 + \dots \quad (1.3.1)$$

This is the Virial equation of state, where the inclusion of an increasing number of B, C, ... etc. terms multiplied by powers of  $\left(\frac{n}{V}\right)^{1,2,\dots}$  can arbitrarily increase the accuracy (although typically one does not see the series go beyond the  $C(T)$  term). At first, it would appear that the Virial is not better than the van der Waals, as both only have  $\sim 2$  additional parameters to rectify the perfect gas law. However, did you notice that the Virial parameters  $B(T)$  and  $C(T)$  are temperature dependent whereas the van der Waals parameters are not? As a result, the Virial is substantially more accurate than the van der Waals equation, which is why we used it to model the compression factor of helium in Figure 1.3D. Clearly the Virial does a good job representing helium gas over a range of temperatures and pressures. As a result, we have demonstrated that a series expansion can always be used to create a better fit to experimental data, although hopefully you already knew that.

### 1.3.1 Residual Volume

We have discussed at length the physical basis for the two van der Waals parameters and how they influence the compressibility factor Z. What about the Virial? Do the  $B(T)$  and  $C(T)$  terms have any meaning like the van der Waal's " $a$ " and " $b$ " constants? Unfortunately, such analysis isn't as straightforward, and we have to develop another method for quantifying the (im)perfections of a gas. In this regard, we introduce the residual volume, which is the difference in the per molar volume  $\left(\frac{V}{n} = V_m\right)$  of a real gas minus the same of a perfect gas under very low pressure (or high volume) conditions, i.e.:

$$\text{res. volume} = (V_{m,\text{real}} - V_{m,\text{perf}}) \quad (1.3.2)$$

The reason that a limit is applied (either  $P \rightarrow 0$  Pa or  $V_m \rightarrow \infty$  m<sup>3</sup>/mol) is that real gases behave much more like a perfect gas under these conditions. Hopefully the reasons are obvious- for a limited number of gas molecules in a very large volume container, they do not have much opportunity to interact nor collide. As a result, it is true that  $\left(\frac{PV_m}{RT}\right) = 1.0$ . However, what about the difference  $\left(V_m - \frac{RT}{P}\right)$ ? This is the definition of the residual volume, and at first it appears that it should be 0 m<sup>3</sup>/mol. Let's check this with a derivation, starting with Equation 1.5:

$$\frac{PV}{nRT} = 1.0 + B(T) \cdot \left(\frac{n}{V}\right) + C(T) \left(\frac{n}{V}\right)^2$$

First, factor  $\frac{RT}{P}$  throughout:

$$\frac{V}{n} = V_m = \frac{RT}{P} + B(T) \cdot \left(\frac{nRT}{PV}\right) + C(T) \frac{n^2 RT}{PV^2}$$

and then bring  $\frac{RT}{P}$  to the left:

$$V_m - \frac{RT}{P} = B(T) \cdot \left(\frac{nRT}{PV}\right) + C(T) \frac{n^2 RT}{PV^2}$$

And apply the limit as follows:

$$\left(V_m - \frac{RT}{P}\right) = \left(B(T) \cdot \left(\frac{RT}{PV_m}\right) + C(T) \frac{RT}{PV_m^2}\right)$$

Now here we have a problem. If  $V_m \rightarrow \infty$  m<sup>3</sup>/mol then  $P \rightarrow 0$  Pa, so what do we do with  $PV_m$ ? Does it get infinitely big, or disappear to 0 Pa•m<sup>3</sup>, or maybe it doesn't change at all? Here, we use the fact that  $\left(\frac{PV_m}{RT}\right) = 1.0$ , which means we can replace every  $PV_m$  with  $RT$ :

$$res. \text{ volume} = \left( B(T) \cdot \left( \frac{RT}{RT} \right) + C(T) \frac{RT}{RT \cdot V_m} \right) = B(T)$$

Since the  $RT$  term is not affected by the limit of increasing volume or equivalently decreasing pressure, the  $B(T)$  term survives while the  $C(T)$  term is removed by the remaining  $V_m$  factor that becomes infinitely large. As a result, we can see that the residual volume of a real gas is not  $0 \text{ m}^3/\text{mol}$ , and in fact it is defined by the Virial  $B(T)$  parameter.

Since we are here discussing residual volume, how about we use the van der Waals equation for the same purpose? Starting with Equation 1.2:  $P = \frac{nRT}{V-n \cdot b} - \frac{n^2 \cdot a}{V^2}$ , first multiply everything by  $\frac{(V-n \cdot b)}{nP}$  as follows:

$$\frac{(V-n \cdot b)}{n} = \frac{RT}{P} - \frac{n \cdot a(V-n \cdot b)}{PV^2}$$

Now do some factoring and note that  $\frac{V}{n} = V_m$ :

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

Rearranging  $\frac{RT}{P}$  and  $b$  with application of the limit yields:

$$\left( V_m - \frac{RT}{P} \right) = res. \text{ volume} = \left( b - \frac{a}{PV_m} - \frac{a \cdot b}{PV_m^2} \right)$$

Here, we run into the same problem of what to do with the multiple  $PV_m$  terms, but as before we will replace them with  $RT$ :

$$res. \text{ volume} = \left( b - \frac{a}{RT} - \frac{a \cdot b}{RTV_m} \right) = b - \frac{a}{RT} \quad \text{\label{1_7_}}$$

Thus  $\frac{a \cdot b}{PV_m^2} \rightarrow 0$  as  $V_m \rightarrow \infty$ . So we see that the difference between a real gas volume and a perfect gas volume is that the real gas has extra space taken up by the gas molecules (as defined by the " $b$ " parameter), while the attractive forces work like gravity as they cause the molecules to coalesce to reduce the volume.

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