

1.8: Another way of dealing with real gases- the virial equation

The van der Waals equation is an improvement on the ideal gas law, but it still has weaknesses. More sophisticated equations (Redlich-Kwong and Peng-Robinson are the two most prominent) use the same basic underpinning of correcting the ideal gas law with terms that represent molecular volume and molecular attraction.

On the other hand, a rawer mathematical approach to describing deviations from ideality is to express those deviations as part of a polynomial series where the constants have less intentional physical meaning, but instead are simply fine-tuned corrections. These types of approaches are called *virial equations*, so named as they are expressions of the force between molecules.

The most fundamental of the virial equations multiplies the right side of the ideal gas law by a power series:

$$PV = nRT \left(1 + \frac{nB}{V} + \frac{n^2C}{V^2} + \frac{n^3D}{V^3} + \dots \right)$$

In this equation, B , C , and D (and all the values that would follow) are dubbed *virial coefficients*. In most practical applications, even a mere single correction using B , also known as the *second virial coefficient*, is sufficient:

$$PV = nRT \left(1 + \frac{nB}{V} \right)$$

Use of the third virial coefficient C and the fourth virial coefficient D , let alone further coefficients, are reserved only for specialized technical applications. (The first virial coefficient is in the first term of the parenthetical correction - simply 1 in all conditions.)

Gas	If $T = 100 \text{ K}$, $B =$	If $T = 273 \text{ K}$, $B =$	If $T = 373 \text{ K}$, $B =$
Argon	$-0.1870 \text{ L mol}^{-1}$	$-0.0217 \text{ L mol}^{-1}$	$-0.0042 \text{ L mol}^{-1}$
Helium	$0.0114 \text{ L mol}^{-1}$	$0.0120 \text{ L mol}^{-1}$	$0.0113 \text{ L mol}^{-1}$
Hydrogen	$-0.0020 \text{ L mol}^{-1}$	$0.0137 \text{ L mol}^{-1}$	$0.0156 \text{ L mol}^{-1}$
Neon	$-0.0060 \text{ L mol}^{-1}$	$0.0104 \text{ L mol}^{-1}$	$0.0123 \text{ L mol}^{-1}$
Nitrogen	$-0.1600 \text{ L mol}^{-1}$	$-0.0105 \text{ L mol}^{-1}$	$0.0062 \text{ L mol}^{-1}$
Oxygen	$-0.1975 \text{ L mol}^{-1}$	$-0.0220 \text{ L mol}^{-1}$	$-0.0037 \text{ L mol}^{-1}$

Table 4: Second virial coefficients for selected gases as a function of temperature.
Data directly from the corresponding table in Monk's *Physical Chemistry*, with units converted.

Note that while B has units of L mol^{-1} , it is *not* the same as the van der Waals constant b and does *not* represent volume of molecules; this constant is an attempt to combine all the information included in the van der Waals a and b constants into a *single* value. For that reason, the meaning behind B is far more dependent on temperature than the van der Waals constants. The value of B for oxygen at 273 K is $-0.0220 \text{ L mol}^{-1}$; however, that value approaches negligibility (at $-0.0037 \text{ L mol}^{-1}$) at 373 K, and becomes far more significant ($-0.198 \text{ L mol}^{-1}$) at 100 K.

It's not listed in the table above, but the value of B for oxygen at 298 K is $-0.0158 \text{ L mol}^{-1}$. If we were to determine the volume correction for our kilogram (or 31.25 mol) of oxygen gas at standard ambient temperature, a solution of the simplified virial equation would give:

$$\begin{aligned}
 PV &= nRT \left(1 + \frac{nB}{V} \right) \rightarrow P = \frac{nRT}{V} \left(1 + \frac{nB}{V} \right) \\
 \rightarrow P &= \frac{(31.25 \text{ mol})(0.082058 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{40.0 \text{ L}} \left(1 + \frac{(31.25 \text{ mol})(-0.0158 \text{ L mol}^{-1})}{40.0 \text{ L}} \right) \\
 \rightarrow P &= 19.1 \text{ atm}(1 - 0.0123) = \mathbf{18.9 \text{ atm}}
 \end{aligned}$$

This is a correction very similar to that given by the van der Waals equation.

Because of the dependence on temperature that the virial coefficients show, virial coefficients are not traditionally tabulated simply. Papers and entire volumes are given over to the calculation of virial coefficients at a range of specific temperatures, and those coefficients are generally derived through gas behavior or empirically determined. Reliable approximations for many applications are genuinely valuable, and worth the price of a scientific text.

It's worth a mention, at the end of this particular discussion, that the quantity n/V turns up *repeatedly* in these equations, in the virial equation in particular. It's convenient to simplify this quantity, and we usually do so by creating a definition called the *molar volume* of a gas:

$$\bar{V} = \frac{V}{n} \text{ units of } \bar{V}: \text{L mol}^{-1}$$

This definition allows us to simplify the virial equation reasonably well:

$$PV = nRT \left(1 + \frac{nB}{V} \right) \rightarrow P \frac{V}{n} = RT \left(1 + \frac{n}{V} B \right) \rightarrow P\bar{V} = RT \left(1 + \frac{B}{\bar{V}} \right)$$

We can also apply this definition to the van der Waals equation, and achieve a similar simplification:

$$\begin{aligned} \left(P + \frac{n^2 a}{V^2} \right) (V - nb) &= nRT \rightarrow \left(P + \frac{n^2 a}{V^2} \right) \left(\frac{V - nb}{n} \right) = RT \\ \rightarrow \left(P + \frac{n^2}{V^2} a \right) \left(\frac{V}{n} - b \right) &= RT \rightarrow \left(P + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT \end{aligned}$$

We will use this definition repeatedly to make our lives easier as we start to dig into the actual discipline of thermodynamics. Be aware that, for clarity's sake, I make a very deliberate nomenclature choice and write the molar quantity with a bar over the symbol. This choice will take other quantities that other textbooks are less clear about and help us understand more deeply.

This page titled [1.8: Another way of dealing with real gases- the virial equation](#) is shared under a [not declared](#) license and was authored, remixed, and/or curated by [Chuck Pearson](#).

- [1.6: Another way of dealing with real gases: the virial equation](#) by [Chuck Pearson](#) has no license indicated.