


## 1.2: Van der Waals Equation

People figured out that the perfect gas law was far from perfect back when horseback riding was still a mode of transportation. In 1881 Johannes van der Waals realized that the perfect gas law can be derived from another set of relationships that govern energy, so long as the gas molecules cannot interact with each other. This also implies that the gas atoms do not collide and that the molecules do not have their own volume. As a result, he inserted two parameters ("a" and "b") to the perfect gas equation to describe gas behavior more realistically:

$$P = \frac{nRT}{V - n \cdot b} - \frac{n^2 \cdot a}{V^2} \quad (1.2.1)$$

This is called a real gas equation and applies to "real gases" as opposed to an "unreal" perfect gas. The "a" and "b" parameters are unique for every gas and are determined from experimental data. But do these constants mean anything? Let's first study the "a" parameter by eliminating "b" (we set it equal to 0 m<sup>3</sup>/mol) and we find that:  $P_{real} \approx \frac{nRT}{V} - \frac{n^2 \cdot a}{V^2}$ . Next, subtract the perfect gas equation  $P_{perfect} = \frac{nRT}{V}$  from it:

$$P_{real} - P_{perfect} \approx \frac{nRT}{V} - \frac{n^2 \cdot a}{V^2} - \frac{nRT}{V} = -\frac{n^2 \cdot a}{V^2}$$

 Therefore, the difference between the van der Waals equation (with b = 0 m<sup>3</sup>/mol) and the perfect gas equation is:  $\Delta P = -\frac{n^2 \cdot a}{V^2}$ . Since the van der Waals "a" parameter is positive for all known gases, this shows that the "a" parameter's role is to make a real gas's pressure less than a perfect gas because  $\Delta P$  is always negative. Notice how the difference  $-\frac{n^2 \cdot a}{V^2}$  can be much bigger if V is small, which happens if you have a lot of gas at a very high pressure. These effects are shown in Figure 1.2, which is the perfect gas pressure and van der Waals pressure for CO<sub>2</sub> under various conditions. It can be seen that the real gas pressure is lower than that predicted by the perfect gas law.

Now imagine that you're at your 1<sup>st</sup> Physical Chemistry exam and are asked to describe why that might be (this is probably going to happen!). Recall that van der Waals knew that gas molecules must not interact with themselves nor occupy any volume for  $PV = nRT$  to work. Would a real gas molecule's ability to interact with itself decrease the real pressure? Or perhaps the real pressure is modulated due to fact that the gas molecules occupy some of the volume (this would likely raise the pressure)? Hopefully your intuition leads you to believe that the "a" parameter is associated with a gas molecule's ability to interact among themselves, which would lower the pressure. This is like gravitational attraction that keeps our solar system together- without gravity all the planets, stars and asteroids would all fly apart from each other as though they were gas molecules at high pressure suddenly released from the container!

Gas	a (kPa · L <sup>2</sup> /mol <sup>2</sup> )	b (L/mol)	P <sub>c</sub> (atm)	T <sub>c</sub> (K)
He	3.46	0.0238	2.23	5.18
H <sub>2</sub>	24.76	0.02661	12.8	33.2
N <sub>2</sub>	137.0	0.0387	33.4	126
Xe	425.0	0.05105	57.6	290
O <sub>2</sub>	138.2	0.03186	49.8	155
CH <sub>4</sub>	228.3	0.04278	45.0	188
CO <sub>2</sub>	364.0	0.04267	73.1	304
H <sub>2</sub> O	553.6	0.03049	218	647

The meaning of the "b" parameter can be determined by unit analysis. This is one reason that units are emphasized here, because you can often use them to answer questions! This also gives us a challenge problem- what are the units of "b" given the following:

$$\frac{nRT}{V - n \cdot b} \propto \frac{J}{m^3 - mol \cdot b}$$

Based on the previous discussion, hopefully you realize the Joule doesn't matter, rather the  $n \cdot b$  term must have units of  $m^3$  (the same as  $V$ ) since they are members of a summation; note subtraction is just the addition of a negative quantity. Some middle school algebra reveals that " $b$ " has units of  $m^3/mol$  and represents the volume of the actual gas molecules. You might have noticed the units of " $b$ " were stated on the previous page- try to pay more attention!

There is another way to determine what " $b$ " represents, which is to find what the volume of the van der Waals gas at high pressure. To derive this, first take the van der Waals equation, bring the " $a$ " term to the right:

$$\left( P + \frac{a \cdot n^2}{V^2} \right) = \frac{nRT}{(V - n \cdot b)}$$

and then multiply by  $V - n \cdot b$  :

$$(V - n \cdot b) \left( P + \frac{a \cdot n^2}{V^2} \right) = nRT$$

Now divide out by the left hand  $P + \frac{a \cdot n^2}{V^2}$  term and take the limit of high  $P$ :

$$(V - n \cdot b) = \frac{nRT}{\left( P + \frac{a \cdot n^2}{V^2} \right)}$$

On the right-hand side, we see that there is a finite  $nRT$  term divided by a very large number ( $P$ ), which makes me think the limit is  $0 m^3$ . Before we make this conclusion we need ask what can  $\frac{a \cdot n^2}{V^2}$  do to mess up the limit? To answer, first let's ask ourselves how can  $P$  get infinitely big? Why, by making  $V$  infinitely small, resulting in  $\frac{a \cdot n^2}{V^2}$  becoming very big (just like  $P$ !). Thus, we can safely conclude that  $\frac{nRT}{\left( P + \frac{a \cdot n^2}{V^2} \right)} = \frac{nRT}{(\infty + \infty)} = 0 m^3$ , and thus:


$$(V - n \cdot b) = 0 m^3$$

or better yet the van der Waals  $b$  term is equal to  $\frac{V}{n}$ , the volume per mole under extremely high pressure. As most gases will solidify is put under enough pressure, and a solid's volume is fully occupied by the "bodies" of the molecules, we now see that " $b$ " is the per molar volume of the actual molecules and is not related to the size of the container ( $V$ ) that they reside in.

**1.2.1 Compressibility Factor.** How necessary is the use of a real gas equation such as the van der Waals? This is the same as asking, how "bad" is the perfect gas law for describing real gases? To answer this question, we introduce a unitless metric called the compressibility factor " $Z$ ":

$$Z = \frac{P_{real}}{P_{perfect}} = \frac{P_{real} V}{nRT} \quad (1.2.2)$$

Compressibility is a fraction for which  $Z = 1.0$  if a real gas behaves like a perfect one. Shown in Figure 1.3A are values for  $Z$  for nitrogen gas over a temperature and pressure range of 140 K to 300 K and 8 atm to 260 atm, respectively. Here we see that  $Z$  can deviate substantially from 1.0, usually being less than 1.0 and reaching the lowest value of 0.406 at 140 K at a perfect gas pressure of 65 atm. How do you interpret these data? For example, a compressibility factor less than 1.0 means that  $P_{real} V$  is less than  $nRT$ , but is it the pressure or volume that is "too small"? Since these measurements were likely made in a thick, solid metal container, the volume of which doesn't vary no matter the temperature and pressure of the gas inside of it, we assign the compressibility factor to pressure. What this means is that, if  $Z = 0.406$ , then the measured real pressure of  $N_2$  gas is 26.4 atm *when it should have been 65 atm* if it behaved like a perfect gas and its pressure was the same as  $\frac{nRT}{V}$ . Likewise, Figure 1.3C shows that helium's compressibility can be much greater than 1.0, and thus the pressure is "too high". As can be seen, real gases can have substantial deviations from perfect gas behavior.

 The van der Waals equation can be used to estimate the compressibility factor. Starting with  $P = \frac{nRT}{V - n \cdot b} - \frac{n^2 \cdot a}{V^2}$ , we multiply both sides by  $\frac{V}{nRT}$ :

$$\frac{PV}{nRT} = Z = \frac{V}{V - n \cdot b} - \frac{a \cdot n}{RTV} \quad (1.2.3)$$

which reveals that  $Z$  is increased by the effect of the molecular volume (the " $b$ " parameter) because " $b$ " is always positive and thus  $\frac{V}{V - n \cdot b} \geq 1.0$ . The attractive forces (the " $a$ " parameter) can only lower  $Z$ . As can be seen in Figure 1.3A and C,  $Z$  is usually less than 1.0 for nitrogen but generally greater than 1.0 for helium. The latter behavior is generally only observed with  $H_2$ , He, and Ne, while all other real gases behave like  $N_2$ . Examination of the van der Waals constants for these gases on Table 1.0 shows that  $H_2$ , He, and Ne have very low " $a$ " values. Thus,  $H_2$ , He, and Ne are more like hard billiard balls that are constantly cracking against each other. This is not true for most real gases like  $N_2$ ,  $CO_2$  and  $CH_4$ ; their behavior is dictated more by their self-attraction via the " $a$ " parameter. Furthermore, note that the low value of  $N_2$ 's  $Z$  seen in Figure 1.3A occurs when the gas is cold and under high pressure, where it is close to liquifying. Of course the perfect gas equation is way off under these conditions! "

Shown in Figure 1.3B are the calculated  $Z$ 's for  $N_2$  gas using the van der Waals equation. As can be seen, this real gas equation generates a reasonable representation of the behavior of  $N_2$ , but it's not perfect. This is because the van der Waals equation ultimately tries to predict very complex, at times quantum mechanical behavior using just two empirically fitted parameters. Of course it isn't perfect! But clearly superior to the perfect gas law, which is represented by a flat plane at  $Z=1.0$ . And good enough for van der Waals to win the Nobel Prize in Chemistry in 1911.

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