Solving van der Waals’ Equation

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September, 1990
Major Revision: September, 1993

1. The Problem with van der Waals’ Equation

Van der Waals’ equation is:

\[
\left( p + \frac{n^2a}{V^2} \right)(V - nb) = nRT , \tag{1}
\]

where \( p \) is the pressure, \( V \) is the volume, \( T \) is the temperature, \( n \) is the number of moles of gas present, \( R \) is the gas constant, and \( a \) and \( b \) are constants that depend upon the gas.

In the usual situation \( a \) and \( b \) are known and can be found in tables. One must watch the units used though. Usually \( a \) is in liter\(^2\) atm mole\(^{-2}\), though occasionally cc’s are used instead of liters. Similarly \( b \) is most often in liter mole\(^{-2}\), though again cc’s are sometimes used. Thus it is usually convenient to work in liter-atm and to take \( R = 0.0820578 \) liter-atm/mole-kelvin.

In a problem, if the volume and temperature were known and the pressure were needed, we simply use:\(^1\)

\[
p = \left( \frac{nRT}{V - nb} \right) - \left( \frac{n^2a}{V^2} \right) . \tag{2}
\]

Or if the pressure and volume were known and the temperature were needed:

\[
T = \left( \frac{1}{nR} \right) \left( p + \frac{n^2a}{V^2} \right)(V - nb) . \tag{3}
\]

Trouble comes when pressure and temperature are known and the volume is wanted. A look at equation (1) shows that \( V \) occurs in two different places. A short trial with pencil and paper demonstrates that equation (1) is not linear in \( V \). Indeed, if equation (1) is multiplied out, what results is:

\[
pV^3 - n(RT + bp)V^2 + n^2aV - n^3ab = 0 , \tag{4}
\]

which is a cubic in \( V \).

\(^{1}\)I know that you can work out these formulas on your own, it just seemed like a good idea to collect them together in one place.
Solving cubics is not as simple as solving quadratics. There is a "cubic formula", but it is quite messy and takes a large amount of work.²

But it is important to remember van der Waals’ equation for the volume is a cubic and cubics always have three roots. One is guaranteed to be real, the other two can be either real or complex. Of course, any root that would be physically meaningful as the volume of a gas would be both real and positive. So we need not be concerned with imaginary roots.³

### 2. Solving van der Waals’ Equation for the Volume – The General Problem

We can rewrite van der Waals’ equation as:

\[
\left(p + \frac{n^2 a}{V^2}\right)(V - nb) - nRT = 0.
\]  

(5)

Now finding a value of \( V \) that fits with given values of \( p \) and \( T \) for a given gas is the problem of finding a \( V \) that makes the left-hand side of equation (5) equal zero. In a more standard mathematical notation we can call the right-hand side of equation (5) \( f(V) \). Then what we want is to find a \( V \) such that

\[
f(V) = 0.
\]  

(6)

This sort of problem is well-known in math. It is the problem of finding a root of equation (6). In the general case \( f(V) \) could be any function. In some few of these cases (linear equations, quadratic equations) an analytic solution can be obtained easily. In others (cubics, quartics), analytic solutions are known, but they are often too messy to use. And in most cases, there is no analytic solution at all.

This sort of problem comes up quite regularly in science. In school we cheat. We usually keep you from seeing equations that can’t be solved analytically. This is unfortunate because it gives students a false view of the world.

But what is to be done when you do come up against a "find the root" problem with no useful analytic solution? Answer: you use numerical approximation. Numerical approximations give answers that can be every bit as accurate as analytical results. The work involved in a numerical approximation usually depends upon how much accuracy is wanted. And there are standard numerical methods.

The standard way of finding roots of equations was developed in the mid 1600’s by Isaac Newton.⁴ The "modern" version was developed by Raphson. The technique is known as Newton-Raphson. It goes like this. Let \( x_i \) be an approximation to a root of \( f(x) = 0 \), then a better approximation is given by:

\[
x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)},
\]  

(7)

where \( f'(x) \) stand for the derivative of \( f(x) \) with respect to \( x \).

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² Those of you who are interested can check the Appendix at the back of this handout for the formula.
³ Which is a break for the good guys.
⁴ You don’t learn about this in school because it is too new for most teachers.
And of course, if $x_{i+1}$ isn’t a good enough result, one can plug it into the right-hand side of equation (7) and calculate $x_{i+2}$, which will be an even better approximation. The process of repeating a calculation cyclically is called iteration.

One disadvantage of the method is that you have to compute a derivative. The advantage of the method is that it is quadratically convergent, which is a fancy way of saying that the number of significant digits in the approximation doubles with every iteration.\(^5\)

Where does one get the first value of $x$? That’s an interesting question. Newton-Raphson does not always work. To have it work you must start out with a guess that is near enough to the actual root of the equation you are trying to solve. In general the best way to do this is to graph the equation, at least roughly. That should give you an approximate root to start with. Here, in solving van der Waals’ equation, we are luckier. We can use the ideal gas law to give us a first approximation.

### 3. Solving van der Waals’ Equation – Details

For van der Waals’ equation $f(V)$ is given by equation (5). Its derivative with respect to $V$ is:

$$f'(V) = p - \frac{an^2}{V^2} + \frac{2abn^3}{V^3},$$

and so the Newton-Raphson formula for van der Waals’ equation is:

$$V_{i+1} = V_i - \frac{p + \frac{n^2a}{V_i^2}(V_i - nb) - nRT}{p - \frac{an^2}{V_i^2} + \frac{2abn^3}{V_i^3}}.$$  \hspace{1cm} (9)

This is easier to use than it looks, but it is impossible to remember.\(^6\)

You can see from equation (9) how this works. If we know the correct value of $V$, placing it into the numerator expression (which is simply van der Waals’ equation) will give 0 as a result. Then nothing will be added to $V_i$ and so $V_{i+1}$ will be the same as $V_i$ (and we will know that our value of $V$ was correct. If we don’t have the correct root, the ratio in equation (9) will "correct" the guess $V_i$ to give a better guess $V_{i+1}$.

Let’s apply this to actual problems.

**Problem 1:** What is the volume of exactly one mole of oxygen gas at a pressure of 10.00 atm. and a temperature of 300.0 K. For oxygen $a$ is 1.360 liter\(^2\) atm/mol\(^2\) and $b$ is 0.003183 liter/mol. Take $R$ to be 0.0820578 liter-atm/mol-K.\(^7\)

We start by finding $V_0$, the "zero’th guess". The ideal gas law gives $V = nRT/p = 2.46$ liters as the volume.\(^7\) Call this value $V_0$. Plugging this value into the numerator of the ratio in equation (9) gives 0.502,  

\(^5\)So if you have two significant figures after the first iteration, you will have four after the second and eight after the third.

\(^6\)And nobody will expect you to remember it either.

\(^7\)There’s no point in carrying a lot of decimal places in the starting value. We know 2.46 isn’t the right
while plugging it into the denominator of the ratio gives 9.78:

\[ V_1 = 2.46 - \frac{0.502}{9.78} = 2.409 \]  

So a better value of \( V \) is 2.409. We now repeat this process using 2.409. Plugging into the numerator gives 0.00463367. (We can see that we are getting closer to zero.) The denominator gives 9.7662691. And

\[ V_2 = 2.409 - \frac{0.00463367}{9.7662691} = 2.40852543 \]  

Since we know that the number of correct digits doubles with each iteration, and we had 3 correct digits (2.40) before, we have at least 6 now, which is certainly more than we need.8

**Problem 2:** Exactly one mole of oxygen gas is kept at a pressure of 100.00 atm and a temperature of 300.0 K. The constants \( a, b \), and \( R \) are the same as in Problem 1.

This will be tougher, since the gas is much less ideal under these high pressure conditions. Nevertheless, we get \( V_0 \), our first approximation, from the ideal gas law: \( V = \frac{nRT}{p} = 0.246 \) atm., so \( V_0 = 0.246 \).

Using this value the numerator in equation 9 is 5.12 (and that’s certainly far from zero!) The denominator is 78.11 and

\[ V_1 = 0.246 - \frac{5.12}{78.11} = 0.1805 \]  

and \( V_1 \) is 0.1805 liters. Repeating this process using 0.1805 as the value of \( V \) gives 0.516118 for the numerator (much closer to zero) and 59.7291 for the denominator. Then:

\[ V_2 = 0.1805 - \frac{0.516118}{59.7291} = 0.171859 \]  

We aren’t there yet. So far there are only two significant digits. We can tell by the fact that 0.516 over 59.7 is 0.0086, so the correction only affects the third decimal place. We need a few more decimal places. So we go ’round again. This time the numerator is 0.0171587 and the denominator is 55.659387, and

\[ V_3 = 0.171859 - \frac{0.0171587}{55.659387} = 0.1715507 \]  

Since the correction is 0.0003, we probably have at least four significant figures, which is surely enough.9

4. The Moral of the Story

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8 The correct 5-digit result is 2.4085 liters.
9 The correct 6-digit answer is 0.171550 liters.
In this course you are going to have to solve van der Waals’ equation for the volume. And later you will use Newton-Raphson for other problems. Wisdom dictates that you practice now, not on a quiz or an exam. Some practice problems follow.

5. Practice Problems

1. Use Newton-Raphson to find the roots of the equation

\[ x^2 - 5.859872 \times + 8.539727 = 0 \]

You can check your answer using the quadratic formula.

2. Find the volume occupied by one mole of water vapor at 500° C and a pressure of 200 atm. For water \( a \) is 5.46 liter 2–atm/mol 2 and \( b \) is 0.0305 liter/mol. To check your work the answer is 0.2527 liters.

3. For benzene, a molecule worshipped by some chemists, \( a \) = 18.00 liter 2–atom/mol 2 and \( b \) is 0.1154 liter/mol. Find the volume of 1.400 moles of benzene vapor at 500°C and a pressure of 40.00 atm. The answer is 1.971 liters.

Appendix

For those of you who are gluttons for punishment, the "standard" way of solving cubics is this: Given the cubic10

\[ x^3 + a_1 x^2 + a_2 x + a_3 = 0 , \]  

(A1)

Compute the quantities \( Q \) and \( R \) from:11

\[ Q = \frac{a_1^3 - 3a_2}{9} \]  

(A2)

and

\[ R = \frac{2a_1^3 - 9a_1 a_2 + 27a_3}{54} . \]  

(A3)

Check to see if \( Q^3 - R^2 \geq 0 \). If this is so the cubic equation has three real roots. They can be found by computing

\[ \theta = \text{arc cos}(R/\sqrt{Q^3}) . \]  

(A4)

The three roots are then:

10 Any cubic can be put into this form by simply dividing through by the coefficient of the \( x^3 \) term.

\[
x_1 = -2\sqrt{Q}\cos\left(\frac{\theta}{3}\right) - \frac{a_1}{3},
\]
\[
x_2 = -2\sqrt{Q}\cos\left(\frac{\theta + 2\pi}{3}\right) - \frac{a_1}{3}, \quad (A5)
\]
\[
x_3 = -2\sqrt{Q}\cos\left(\frac{\theta + 4\pi}{3}\right) - \frac{a_1}{3}.
\]

If \(Q^3 - R^2 < 0\), then the cubic has only one real root. This is given in terms of \(S\) by:

\[
x_1 = -\text{sgn}(R) \left[S + \frac{Q}{S} \right] - \frac{a_1}{3}, \quad (A6)
\]

where \(S\) is:

\[
S = \left(\sqrt{R^2 - Q^3} + |R| \right)^{1/3}, \quad (A7)
\]

and \(\text{sgn}(R)\) is +1 if \(R\) is positive, -1 if \(R\) is negative, and 0 if \(R\) is zero.\(^{12}\)

\(^{12}\) I told you that cubics were a mess!