

VIRIAL EXPANSION FOR A GAS

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 1.17.

The ideal gas law isn't entirely accurate for any real gas. For low density gases, one way of accounting for deviations from the ideal gas law is to use a *virial expansion*:

$$(1) \quad PV = nRT \left[1 + \frac{B(T)}{(V/n)} + \frac{C(T)}{(V/n)^2} + \dots \right]$$

where B and C are the virial coefficients, and depend on the particular gas we're modelling. For nitrogen molecules N_2 the measured values of B are

T (K)	B (m^3/mol)	V/n (m^3/mol)	$B(T)/(V/n)$
100	-160×10^{-6}	0.0082	-0.0195
200	-35×10^{-6}	0.0164	-0.00213
300	-4.2×10^{-6}	0.0246	-0.00017
400	9.0×10^{-6}	0.0328	0.000274
500	16.9×10^{-6}	0.0410	0.000412
600	21.3×10^{-6}	0.0492	0.000433

Using the ideal gas law and the gas constant $R = 8.31$ J/K to get values for V/n at each temperature gives the third column in the table, and then we can use these values to calculate the $B/(V/n)$ terms in the fourth column. [Note that I've converted Schroeder's values to SI units.] The corrections are very small so the ideal gas law should work well under these conditions.

As to why B is negative for low temperatures and positive for high temperatures, it is known that gas molecules feel a weak attraction when fairly close to each other. At low temperatures, the molecular speed is lower, so this attraction would have a chance to be more strongly felt. Thus the molecules would tend to be closer to each other than if they didn't interact, resulting in a slightly smaller volume. A negative value of B (at a given P and T) means a smaller volume.

For higher temperatures, the molecules are moving too fast for this attraction to have any effect, so molecules simply bounce off each other. Because the molecules have a non-zero volume (as opposed to the point molecules

assumed by the ideal gas law), a slightly larger volume is needed at a given (high) temperature and pressure.

Another equation of state (that is, a relation between P , V and T) is the van der Waals equation:

$$(2) \quad \left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where the parameters a and b are constant for a given gas. To compare this to the virial expansion above, we can write this as

$$(3) \quad \left(P + \frac{an^2}{V^2}\right)(V - nb) = \left(P + \frac{an^2}{V^2}\right)V \left(1 - \frac{nb}{V}\right)$$

$$(4) \quad PV = nRT \left(1 - \frac{nb}{V}\right)^{-1} - \frac{an^2}{V}$$

$$(5) \quad = nRT \left[\left(1 - \frac{b}{V/n}\right)^{-1} - \frac{a}{RT(V/n)} \right]$$

By Taylor-expanding the first term in brackets, assuming $bn/V \ll 1$, we get

$$(6) \quad PV \approx nRT \left[1 + \frac{b}{V/n} + \frac{b^2}{(V/n)^2} - \frac{a}{RT(V/n)} \right]$$

$$(7) \quad = nRT \left[1 + \frac{1}{V/n} \left(b - \frac{a}{RT}\right) + \frac{b^2}{(V/n)^2} \right]$$

Comparing with 1 we see that the van der Waals model predicts

$$(8) \quad B(T) = b - \frac{a}{RT}$$

$$(9) \quad C(T) = b^2$$

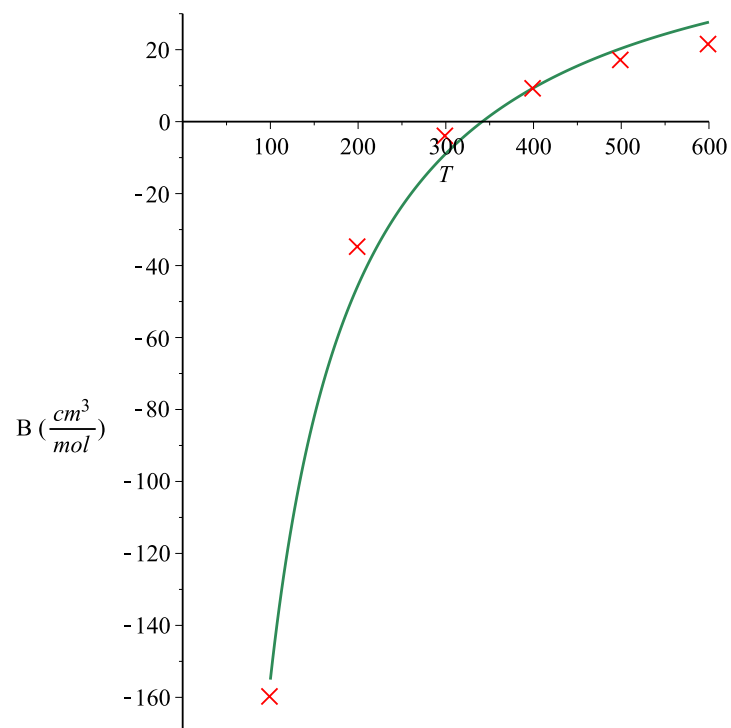
By fitting the curve 8 to the data in the table above, we can get estimates for a and b . I used Maple's *Fit* function (which does a least squares fit), with the result:

$$(10) \quad a = 0.0219 \text{ J m}^3 \text{ mol}^{-2}$$

$$(11) \quad b = 6.42 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

Comparing the value of b with the values of V/n in the above table, we see that our assumption of $bn/V \ll 1$ is consistent, so we're safe.

The following plot illustrates how good the fit is:



The green curve is the van der Waals fit 8 and the red crosses are the data from the table above. [Note that B is plotted using Schroeder's units, which are just SI units multiplied by 10^6 .] The fit is actually fairly good, so the van der Waals equation is a decent model for these data.