

## VIRIAL EXPANSION FOR A GAS

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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*:

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

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	$-160 \times 10^{-6}$	0.0082	-0.0195
200	$-35 \times 10^{-6}$	0.0164	-0.00213
300	$-4.2 \times 10^{-6}$	0.0246	-0.00017
400	$9.0 \times 10^{-6}$	0.0328	0.000274
500	$16.9 \times 10^{-6}$	0.0410	0.000412
600	$21.3 \times 10^{-6}$	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. 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:

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

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

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

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

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

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

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

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

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

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

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

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:

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

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

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.

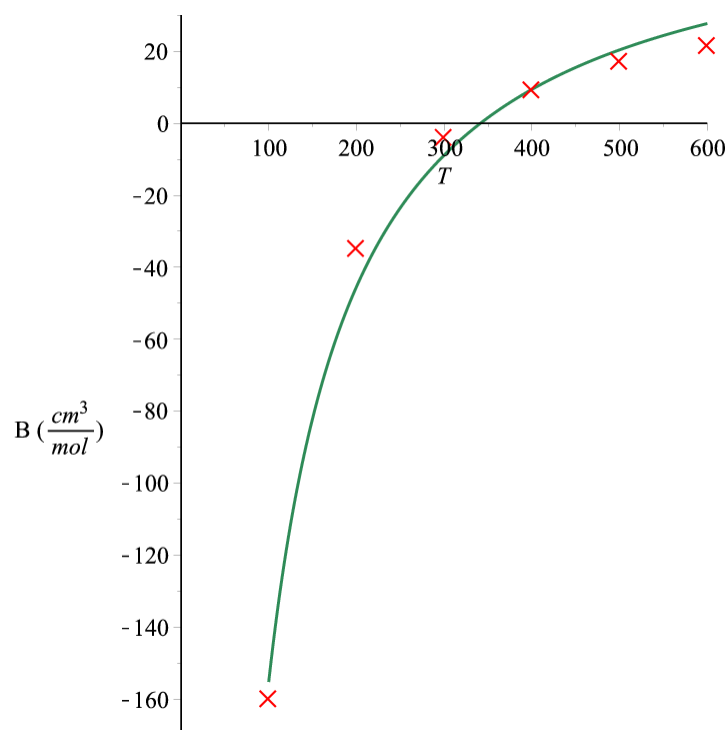


FIGURE 1. Van der Waals fit for virial coefficient  $B$ .

Fig. 1 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. The fit is actually fairly good, so the van der Waals equation is a decent model for these data.