

IMPERFECT GASES¹

At the limit of low densities, all gases approach ideal-gas behavior:

$$P = \rho kT \quad (1)$$

This equation can be easily derived for a monoatomic gas in which the intermolecular potential can be ignored. Physically, this means that the particles spend practically all their time away from each other and do not "feel" the presence of other particles. Consider the canonical partition function of N monoatomic particles contained in a volume \underline{V} at temperature T :

$$Q = \frac{1}{N! h^{3N}} \int \dots \int e^{-\beta H} dp_1 dp_2 \dots dp_N dr_1 dr_2 \dots dr_N \quad (2)$$

Since H is of the form

$$H = \frac{1}{2m} \sum_{n=1}^N (p_{xn}^2 + p_{yn}^2 + p_{zn}^2) + \underline{U}(x_1, y_1, z_1, \dots, z_n)$$

we can immediately integrate equation (2) and obtain

$$Q = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N \quad (3)$$

where Z_N is the configurational integral

$$Z_N = \int \dots \int e^{-\underline{U}_N/kT} dr_1 dr_2 \dots dr_N \quad (4)$$

If we can set $\underline{U}_N=0$ in the configurational integral, then $Z_N = \underline{V}^N$ and $Q = q^N/N!$ where $q(\underline{V}, T) = (2\pi mkT/h^2)^{3/2} \underline{V}$. The key point is that it is q being of the form $f(T) \cdot \underline{V}$ that leads directly to the ideal gas equation of state. Although we have discussed only the case of monoatomic gases here, the same result holds true for polyatomic gases. This is easily proved at the expense of introducing a number of angular interactions.

As the density of the gas is increased, the particles are closer on the average, and the intermolecular potential becomes nonnegligible. Thus, the configuration integral is no longer simply \underline{V}^N , and the ideal-gas equation of state is not obtained as the equation of state of the gas. Of course, it is well known experimentally that the real gases exhibit deviations from ideal gas behavior as the density is increased. A large number of empirical and semi-empirical equations of state have been constructed to describe the deviations from the simple ideal gas law. The most fundamental of these, in the sense that it has the most sound theoretical foundation, is the so-called virial equation of state. The virial equation expresses the deviations from ideal behavior as an

¹ Material in this section is based on Chapter 12 of D.A. McQuarrie, "Statistical Thermodynamics", Harper and Row, 1976.

infinite power series in ρ :

$$\frac{P}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots \quad (5)$$

The quantities $B_2(T)$, $B_3(T)$, ... are called the second, third, ... virial coefficients, respectively, and depend only on the temperature and on the particular gas under consideration, but not on pressure or density. In the following, we will derive expression for the virial coefficients in terms of the intermolecular forces. Before going on to this, it is helpful to consider Table 1, which gives the contribution of the first few terms in the virial expansion to $P/\rho kT$. The data are for argon at 25°C. The contributions of the remaining terms are shown in parentheses. It can be seen that the second and third virial coefficients alone give most of $P/\rho kT$ up to pressures approaching 100 atm. This is only because at 25°C Ar is at a reduced temperature of $T/T_c \approx 2.0$, far above the critical point. At lower reduced temperatures, the contributions of higher order terms becomes much more significant at lower pressures.

Table 1. The contribution of the first few terms in the virial expansion of $P/\rho kT$ for Ar at 25°C

P (atm)	$P/\rho kT$
	$1 + B_2\rho + B_3\rho^2 + \dots$ (remainder)
1	$1 - 0.00064 + 0.00000 + \dots$ (+0.00000)
10	$1 - 0.00648 + 0.00020 + \dots$ (-0.00007)
100	$1 - 0.06754 + 0.02127 + \dots$ (-0.00036)
1000	$1 - 0.38404 + 0.68788 + \dots$ (+0.37232)

THE VIRIAL EQUATION OF STATE FROM THE GRAND PARTITION FUNCTION

The grand partition function can be written as

$$\Xi(\underline{V}, T, \mu) = \sum_{N=0}^{\infty} Q(N, \underline{V}, T) e^{\mu N/kT} \quad (6)$$

When $N = 0$, the system has only one state with $\underline{U}=0$, and so $Q(N=0, \underline{V}, T) = 1$. This allows us to write equation (6) as

$$\Xi(\underline{V}, T, \mu) = 1 + \sum_{N=1}^{\infty} Q_N(\underline{V}, T) e^{\mu N/kT} = 1 + \sum_{N=1}^{\infty} Q_N(\underline{V}, T) \lambda^N \quad (7)$$

Where $\lambda = e^{\mu/kT}$, $Q_N(\underline{V}, T) = Q(N, \underline{V}, T)$. From the section on Legendre transforms, we have that

$$\underline{PV} = kT \ln \Xi \quad (8)$$

From the same section, the average number of molecules in the system is:

$$N = kT \left(\frac{\partial \ln E}{\partial \mu} \right)_{\underline{V}, T} = \lambda \left(\frac{\partial \ln E}{\partial \lambda} \right)_{\underline{V}, T} \quad (9)$$

Thus we have the pressure and essentially the density as functions of E . The standard procedure to eliminate E between these two quantities is to obtain a power series for $\ln E$ in some convenient parameter and then to eliminate this parameter between equations (8) and (9). The most obvious choice for the expansion parameter is λ , since in equation (7), E is already a power series in this parameter (which is related to our familiar chemical engineering fugacity). From equation (7), expanding $\ln E$ around $E=1$ (which corresponds to $\lambda=0$):

$$\begin{aligned} \underline{PV}/kT &= \ln E \approx \ln 1 + (\partial \ln E / \partial E)_{E=1} \cdot (E-1) + \frac{1}{2} (\partial^2 \ln E / \partial E^2)_{E=1} \cdot (E-1)^2 + \dots = \\ &= 0 + (1/E)_{E=1} \cdot (E-1) + \frac{1}{2} (-1/E^2)_{E=1} \cdot (E-1)^2 = \\ &= 1 \cdot (E-1) - 1/2 \cdot (E-1)^2 + \dots = \\ &= (Q_1 \lambda + Q_2 \lambda^2 + \dots) - 1/2 \cdot (Q_1^2 \lambda^2 + \dots) = Q_1 \lambda + (2Q_2 - Q_1^2)/2 \cdot \lambda^2 \end{aligned} \quad (10)$$

From equation (9), using the expansion in (10) :

$$N = \rho \underline{V} = \lambda \cdot (Q_1 + 2\lambda \cdot (2Q_2 - Q_1^2)/2 + \dots) = Q_1 \lambda + (2Q_2 - Q_1^2) \lambda^2 + \dots \quad (11)$$

Now, let us expand P as in equation (5), using (11) to express the density ρ :

$$\underline{PV}/kT = \rho \underline{V} + B_2(T) \rho^2 \underline{V} + \dots = Q_1 \lambda + (2Q_2 - Q_1^2) \lambda^2 + B_2(T) Q_1^2 \lambda^2 / \underline{V} + \dots \quad (12)$$

Comparing equation (12) to equation (10), the terms of order λ^2 must be equal:

$$B_2(T) = - \frac{2Q_2 - Q_1^2}{2Q_1^2 / \underline{V}} \quad (13)$$

or, in terms of the configurational integrals, $Z_1 = \underline{V}$ and $Z_2 = 2! (\underline{V}/Q_1)^2 Q_2$

$$B_2(T) = - \frac{Z_2 - Z_1^2}{2\underline{V}} \quad (14)$$

We could have carried out the expansions to a higher order in λ , to obtain expressions for the third and higher order virial coefficients in terms of the corresponding configurational integrals. The result for the third virial coefficient is give below without proof:

$$B_3(T) = - \frac{1}{3\underline{V}^2} \left(\underline{V} (Z_3 - 3Z_2 Z_1 + 2Z_1^3) - 3(Z_2 - Z_1^2)^2 \right) \quad (15)$$

The configurational integrals that appear in equations (14) and (15) can, in principle, be evaluated from information on the intermolecular forces.

For example,

$$Z_2 = \iint e^{-\underline{U}_2/kT} d\mathbf{r}_1 d\mathbf{r}_2 \quad (16)$$

where \underline{U}_2 is the potential for two particles. For monoatomic particles it is reasonable to assume (as we have already suggested in the intermolecular forces section) that $\underline{U}_2(\mathbf{r}_1, \mathbf{r}_2) = \underline{U}(r_{12})$ where $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$. Note that we don't have to invoke the assumption of pair-wise additivity yet, since the integral in equation (16) truly refers to two isolated particles. Equation (14) can then be written as:

$$B_2(T) = - \frac{1}{2V} \iint [e^{-\beta \underline{U}(r_{12})} - 1] d\mathbf{r}_1 d\mathbf{r}_2 = - \frac{1}{2V} \int d\mathbf{r}_1 \int [e^{-\beta \underline{U}(r_{12})} - 1] d\mathbf{r}_{12}$$

The integration with respect to \mathbf{r}_1 will just give V . The other integration can be performed by changing to spherical coordinates:

$$B_2(T) = - 2\pi \int_0^\infty [e^{-\beta \underline{U}(r)} - 1] r^2 dr \quad (17)$$

Equation (17) shows that once the intermolecular potential is known, the second virial coefficient can be calculated as a function of temperature. For example, for some simple potentials:

(a) the hard-sphere potential

$$\begin{aligned} \underline{U}(r) &= \infty & r < \sigma \\ \underline{U}(r) &= 0 & r \geq \sigma \end{aligned}$$

$$B_2(T) = - 2\pi \int_0^\sigma (-r^2) dr = \frac{2\pi\sigma^3}{3} \quad \{\text{independent of temperature}\} \quad (18)$$

(b) the square-well potential

$$\begin{aligned} \underline{U}(r) &= \infty & r < \sigma \\ \underline{U}(r) &= -\varepsilon & \sigma \leq r < \lambda\sigma \\ \underline{U}(r) &= 0 & r \geq \lambda\sigma \end{aligned}$$

$$B_2(T) = b_0 (1 - (\lambda^3 - 1) (e^{\beta\varepsilon} - 1)) \quad \text{where } b_0 = 2\pi\sigma^3/3 \text{ (the hard-sphere } B_2) \quad (19)$$

(c) the Lennard-Jones potential

The integration for the second virial coefficient for the Lennard-Jones potential cannot be performed analytically. In doing this, it is convenient to introduce *reduced parameters*, namely a reduced distance $r^* = r/\sigma$ and a reduced temperature $T^* = kT/\varepsilon$. Using these parameters, it can be shown that the second virial coefficient for the Lennard-Jones potential is

$$B_2^*(T^*) = B_2(T^*)/b_0 = -3 \int_0^{\infty} \left(\exp\left\{ -\frac{4}{T^*} (r^{*-12} - r^{*-6}) \right\} - 1 \right) r^{*2} dr^* \quad (20)$$

Second virial coefficients can also be experimentally measured to within a few percent. Figure 3.6-1 (from J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, "Molecular Theory of Gases and Liquids". Wiley, NY 1954) shows some experimental second virial coefficients versus temperature. From the figure, it would appear that the Lennard-Jones potential does an excellent job in reproducing the experimentally measured second virial coefficients of several gases. Unfortunately, this does not mean that the Lennard-Jones potential is a "good" potential. As can be seen in Figure 3.9-3 (*op.cit.*), the same good agreement between the experimentally measured second virial coefficients and those theoretically calculated can also be obtained from several other potentials with different forms. The second virial coefficient is not very sensitive to the details of the intermolecular interactions.

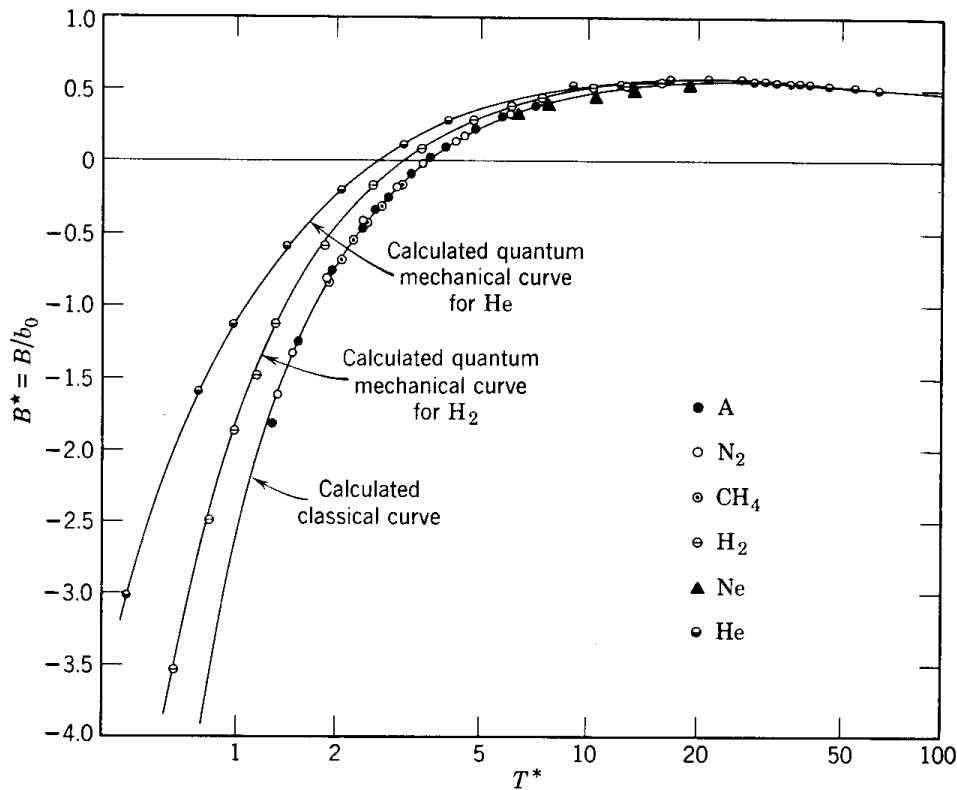


Fig. 3.6-1. The reduced second virial coefficient for the Lennard-Jones potential. The classical curve of $B^*(T^*)$ is shown here along with the experimental points for several gases. Also shown are the curves for hydrogen and helium, which have been calculated by quantum mechanics according to § 6.5b, c. We can see the extent to which quantum deviations are important for these gases. (From R. J. Lunbeck, Doctoral Dissertation, Amsterdam, 1950.)

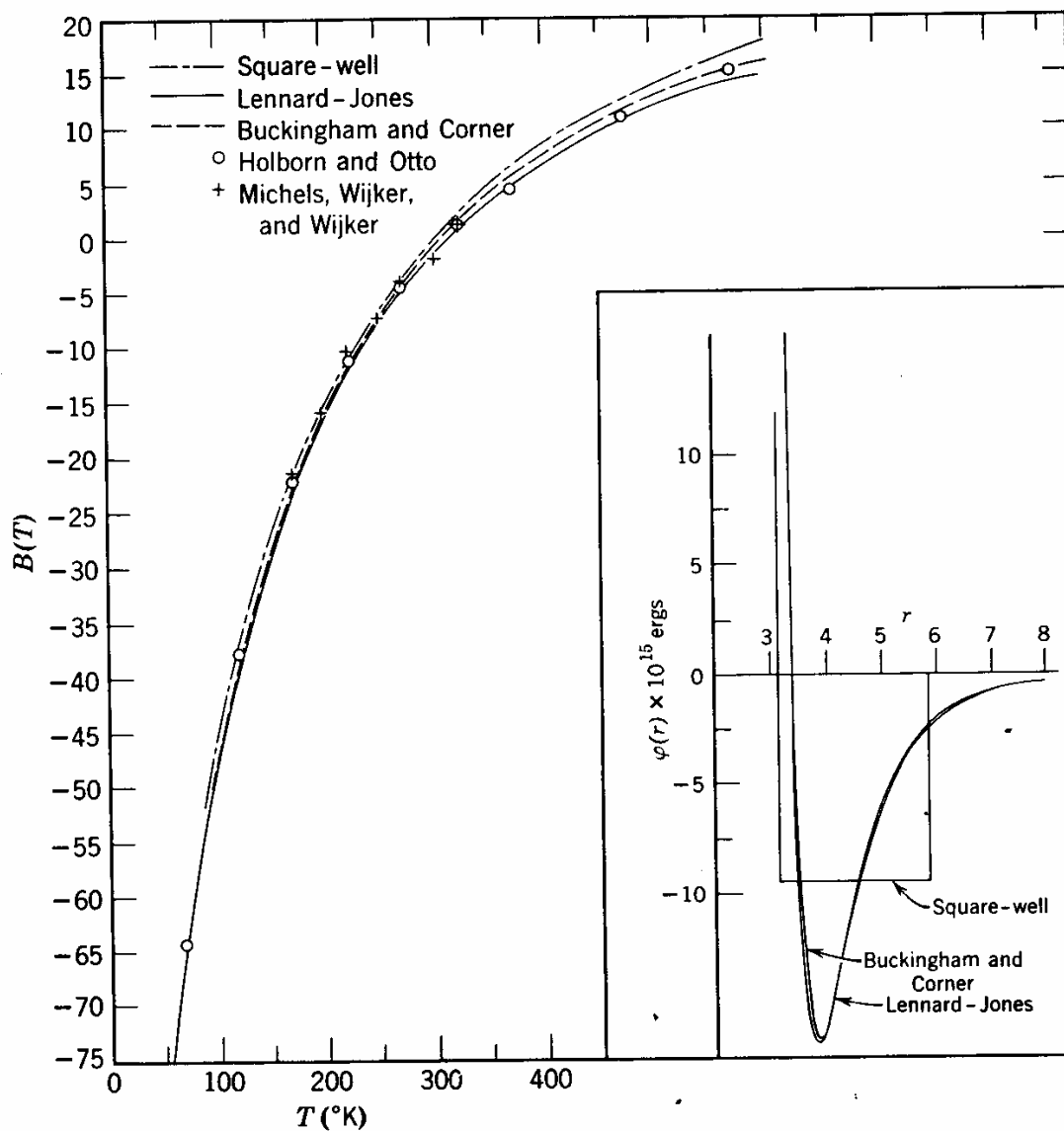


Fig. 3.9-3. Second virial coefficients for *argon* calculated for several molecular models. The potential functions obtained from the experimental $B(T)$ data are also shown. The experimental data are those of L. Holborn and J. Otto, *Z. Physik*, **33**, 1 (1925), and A. Michels, Hub. Wijker, and Hk. Wijker, *Physica*, **15**, 627 (1949).