In eq (58), the coefficient of ρ is the second virial coefficient, the coefficient of ρ^2 is the third virial coefficient, etc.

The second virial coefficient was calculated from eq (58). These coefficients, as functions of temperature are listed in table 13. A comparison between the second virial coefficient calculated by using the virial equation of state (58) and other published data is shown in figure 18.

Except for the data of Kerr [39], figure 18 illustrates that eq (58) represents the second virial coefficients within the uncertainty of the data for temperatures from about 120 to 300 K. Kerr's virial data do not appear to have the precision of the other data sources. For temperatures below 120 K, eq (58) appears to predict virial coefficients which are about 2 percent high. Fender and Halsey [40] estimate their error to be about 1.5 percent, and it is therefore concluded that eq (58) is a satisfactory representation of the virial coefficient data.

TABLE 13. *Second virial coefficients as calculated from virial equation of state (58)*

Temp. K	B	Temp. K	B
90	−215.22	200	−47.18
100	−180.09	210	−42.20
110	−152.39	220	−37.79
120	−130.32	230	−33.86
130	−112.47	240	−30.33
140	− 97.84	250	−27.15
150	− 85.69	260	−24.27
160	− 75.47	270	−21.65
170	− 66.78	280	−19.26
180	− 59.31	290	−17.07
190	− 52.83	300	−15.05

B has units of cm³/mol.

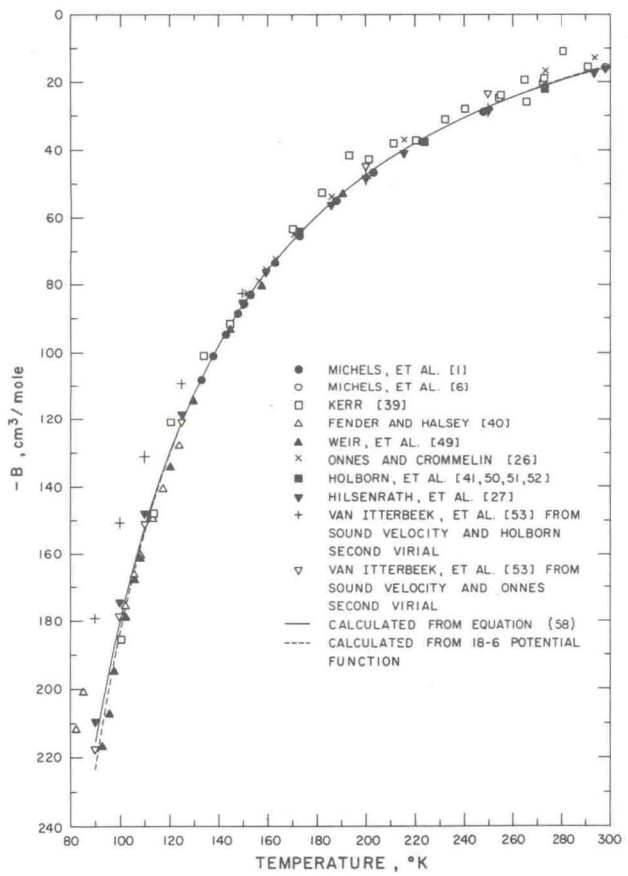

FIGURE 18. *Comparison of second virial coefficients.*

The second virial coefficient may also be theoretically calculated if a mathematical model for the intermolecular force potential is selected. A number of force potentials have been advanced and some of these are discussed in Hirschfelder, Curtiss, and Bird [38] and Gosman [22].

The Lennard-Jones 12–6 model for the potential function is the one most commonly used and was therefore investigated. The expression for the energy for the 12–6 potential is

$$E=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]. \tag{59}$$

Using eq (59), the expression for the reduced second virial coefficient is obtained as illustrated by Gosman [22]:

$$B^*=\sum_{k=0}^{\infty}\left[-\frac{2^{\left(\frac{2k+1}{2}\right)}}{4k!}\,\Gamma\left(\frac{2k-1}{4}\right)\right]T^{*\left(-\frac{2k+1}{4}\right)}. \tag{60}$$

With eq (60) and the equations

$$T^*=\frac{kT}{\epsilon}$$

$$b_0=\frac{B}{B^*}$$

$$b_0=\frac{2}{3}\pi N\sigma^3, \tag{61}$$

the two parameters ϵ and σ were obtained by the method described in Gosman [22].

It was found that the two parameters, ϵ and σ, of the 12–6 potential are not truly constants, but are somewhat temperature dependent. It was also found that the higher temperature isotherms (about 300 K) are relatively insensitive to variations in the parameters. At the lower temperatures, however, relatively small variations in the parameters result in large variations in the second virial coefficient. This effect was demonstrated for argon by Gosman [22] and shown to be a general property of the relationship between second virial coefficients and potential functions by Hanley and Klein [44].

For the temperature range of 90 to 300 K a set of parameters for the Lennard-Jones 12–6 potential was determined to be

$$\epsilon/k=112.4\text{ K}$$

$$b_0=57.7\text{ cm}^3/\text{mol}.$$

Using these parameters, the mean deviation in B from values calculated by eq (58) was 0.78 cm³/mol.

It is of interest to compare the values of these parameters with values determined by other sources. Holborn and Otto [41] found $\epsilon/k = 122$ and $b_0 = 49.58$ for temperatures between 173 and 673 K. Michels, Wijker, and Wijker [6] found $\epsilon/k = 119.8$ and $b_0 = 49.8$ for temperatures between 273 and 423 K. Since the latter two sets of parameters were obtained for relatively high temperature data, it is expected that the value of ϵ/k would be larger than that obtained in this evaluation.

Since the 12–6 potential appears to be satisfactory for limited temperature ranges only, other forms of the potential function were investigated. Using the basic technique developed by Hanley [42] the family of "m-6" functions was evaluated along with the Kihara potential function. The "m-6" functions were calculated by using the values of the reduced second virial coefficients as presented by Klein [43]. The results of these calculations are shown in figure 19.

Figure 19 shows the deviations between second virials as calculated by the various potential functions and those calculated by the virial eq (58). The deviations in second virial for the 12–6, 15–6, 18–6, and Kihara potential functions are all illustrated in figure 19. It is noted that the Kihara and the 15–6 functions are almost identical over the whole temperature range. This similarity between potential functions is discussed by Hanley and Klein [44]. For the temperature range of 90 to 300 K the set of parameters for the Kihara potential was determined to be

$$\epsilon/k = 125 \text{ K}$$
$$\rho_0 = 3.711 \text{ Å}$$
$$a = 0.080 \text{ Å}.$$

Using these values for the Kihara potential, the mean deviation in B from values calculated by eq (58) was 0.53 cm³/mol.

The 18–6 potential shows a negligibly small deviation in second virial above 120 K. Below 120 K, figure 19 shows that the virials calculated by the 18–6 function deviate from those calculated by eq (58). However, this was the temperature range where eq (58) predicted virials which were 2 percent too large. A comparison of the virials calculated by the 18–6 function with the original data shows that the 18–6 function predicts the virial coefficients to about the uncertainty of the data. The 18–6 function is also shown in figure 19 to illustrate this point.

The parameters for the 18–6 function were determined to be

$$\epsilon/k = 157.5 \text{ K}$$
$$\sigma = 3.28 \text{ Å}.$$

Using these values for the 18–6 function, and omitting the deviations below 120 K, the mean deviation in B is 0.14 cm³/mol.

A final calculation was made for the second virial coefficient to determine the corrections due to quantum effects. The relationships which were used to calculate these second virials with quantal corrections for both the 12–6 and the Kihara potentials are given by Hirschfelder et al. [38]. The results indicated that the quantal corrections are a fraction of one percent, even at the lower temperatures. The magnitude of the quantal correction is within the uncertainty of the published experimental data.

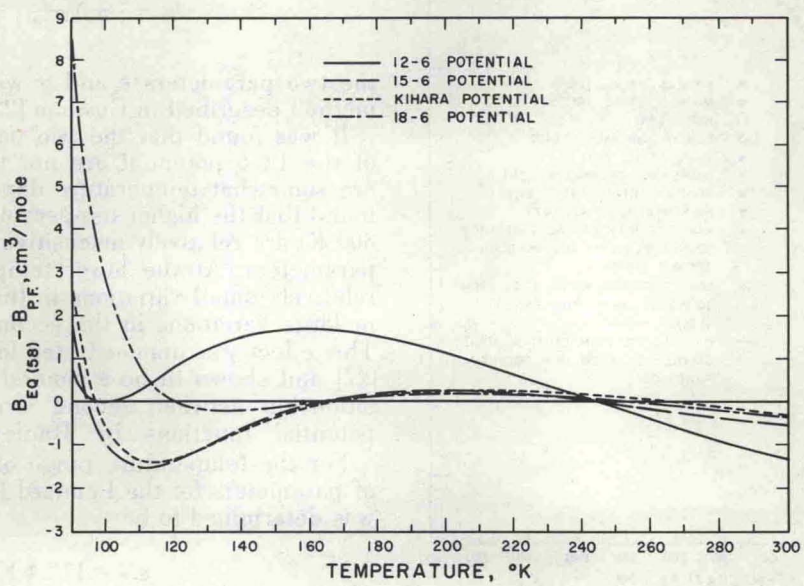

FIGURE 19. *Potential function comparison.*