

Intermolecular Forces in Air¹

Abraham S. Friedman

The intermolecular force constants for a 6-12 Lennard-Jones potential model have been computed for air from second virial coefficients derived from experimental pressure-volume-temperature measurements. Nitrogen:oxygen interaction second virial coefficients and interaction force constants have also been derived.

The following symbols are used throughout the paper:

- Z = Compressibility factor, Pv/RT , dimensionless.
 P = Absolute pressure.
 v = Molar volume, cm^3/mole .
 R = Universal gas constant, in units of Pv/T .
 T = Absolute temperature. The triple point of water is defined as $T = 273.16^\circ\text{K}$.
 B = Second virial coefficient, cm^3/mole .
 C = Third virial coefficient, $\text{cm}^6/\text{mole}^2$.
 D = Fourth virial coefficient, $\text{cm}^9/\text{mole}^3$.
 E = Fifth virial coefficient, $\text{cm}^{12}/\text{mole}^4$.
 ϵ_0 = Maximum energy of binding between a pair of molecules with a Lennard-Jones potential.
 k = Boltzmann's constant.
 N_i = Mole fraction of the i th component.
 b = Lennard-Jones interaction parameter, $\frac{2}{3} \tilde{N} \pi d^3$, in units of molar volume.
 \tilde{N} = Avagadro's number.
 d = Collision diameter of a pair of molecules at zero energy of Lennard-Jones interaction.
 Å = Angstrom units ($\equiv \text{cm}^{-10}$).
 ϵ = Potential energy of two interacting molecules.
 r = Separation between centers of two interacting molecules.
 r_0 = Collision diameter of a pair of molecules at maximum energy, ϵ_0 , of Lennard-Jones interaction.

Compressibility factors for dry air have been determined experimentally and are reported elsewhere [1].² By fitting the P-v-T data to a Kamerlingh-Onnes virial equation of state

$$Z = \frac{Pv}{RT} = 1 + B/v + C/v^2 + D/v^3 + E/v^4 \quad (1)$$

the virial coefficients B , C , D , and E were determined at various temperatures in the region between the critical and 0°C . These are tabulated in table 1.

The second virial coefficients of nonpolar mixtures can be derived, to a good approximation, from the force constants of the pure components [2, 3]. If we assume that the intermolecular forces of the pure constituents of dry air (N_2 , O_2 , and A) can be described by a Lennard-Jones model, then we may define pseudoforce constants for the air mixture:

$$(\epsilon_0/k)_{\text{mix}} = \sum_i N_i (\epsilon_0/k)_i \quad (2)$$

and

$$b_{\text{mix}} = \frac{2}{3} \pi \tilde{N} (d)_{\text{mix}}^3 = \frac{2}{3} \pi \tilde{N} (\sum_i N_i d_i)^3. \quad (3)$$

If we assume that the air mixture has the composition 78.2 percent of N_2 , 20.8 percent of O_2 , and 1.0 percent of A (cf. [1]), and the N_2 , O_2 , and A can be represented by a 6-12 Lennard-Jones intermolecular potential function with force constants:

$$(\epsilon_0/k)_{\text{N}_2} = 95.93^\circ, \quad (d)_{\text{N}_2} = 3.69 \text{ Å} \quad [3, 4]$$

$$(\epsilon_0/k)_{\text{O}_2} = 118.0^\circ, \quad (d)_{\text{O}_2} = 3.46 \text{ Å} \quad [5]$$

and

$$(\epsilon_0/k)_{\text{A}} = 119.5^\circ, \quad (d)_{\text{A}} = 3.42 \text{ Å}, \quad [6]$$

then, from eq (2) and (3), $(\epsilon_0/k)_{\text{air}} = 100.8^\circ$ and $b_{\text{air}} = 60.82 \text{ cm}^3/\text{mole}$.

These 6-12 Lennard-Jones pseudoforce constants can then be used to compute the values of the second virial coefficients for air at various temperatures. The values thus computed are in good agreement with the experimentally determined second virial coefficients [1].

Table 2 compares the calculated and experimental values of B .

The second virial coefficient of a binary gas mixture can be expressed in terms of the second virial coefficients of the constituent gases and an interaction coefficient related to collisions of the unlike molecules.

$$B_{\text{mix}} = \sum_i \sum_j N_i N_j B_{ij}. \quad (4)$$

We may then write for air, noting that $B_{12} \equiv B_{21}$,

$$B_{\text{air}} = (0.79)^2 B_{\text{N}_2} + (0.21)^2 B_{\text{O}_2} + 0.3318 B_{12}. \quad (5)$$

Rearranging:

$$B_{12} = B_{\text{N}_2:\text{O}_2} = (B_{\text{air}} - 0.6241 B_{\text{N}_2} - 0.0441 B_{\text{O}_2}) / 3.014 \quad (6)$$

Using the P-v-T data of Friedman et al., for B_{air} [1], of Friedman for B_{N_2} [3], and the tabulation of Hilsenrath et al., for B_{O_2} [6], the $\text{N}_2:\text{O}_2$ interaction second virial coefficients as a function of temperature may be calculated from eq (6). These are

¹ This research was supported, in part, by the Airborne Equipment Division of the Navy Bureau of Aeronautics.

² Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Virial coefficients of air*

<i>T</i>	<i>B</i> ^a	<i>C</i>	<i>D</i>	<i>E</i>
° <i>K.</i>	<i>cm</i> ³ / <i>mole</i>	<i>cm</i> ⁶ / <i>mole</i> ²	<i>cm</i> ⁹ / <i>mole</i> ³	<i>cm</i> ¹² / <i>mole</i> ⁴
273.15	-12.57	0.7343×10 ³	0.1468×10 ⁶	-0.0688×10 ⁸
250	-19.30	.7646	.1836	-.1011
200	-38.20	1.6303	-.0116	.0345
175	-55.54	2.5492	-.0442	.01986
150	-76.36	3.3923	-.1101	.04184

^a The estimated standard deviation of the second virial coefficients, *B*, vary from 4 to 15 percent of the value of the coefficients. The standard deviations of the other coefficients are a large fraction of the value of the coefficients.

TABLE 2. *Second virial coefficient of air*

<i>T</i>	<i>B</i>	
	Calculated	Experimental
° <i>K.</i>	<i>cm</i> ³ / <i>mole</i>	<i>cm</i> ³ / <i>mole</i>
273.15	-13.4	-12.57
250	-19.6	-19.30
200	-38.9	-38.20
175	-53.3	-55.54
150	-74.1	-76.36

TABLE 3. *Nitrogen: oxygen interaction second virial coefficients*

<i>T</i>	<i>B</i> _{N₂:O₂}
° <i>K.</i>	<i>cm</i> ³ / <i>mole</i>
273.15	-17.5
250	-24.0
200	-44.0
175	-61.3
150	-84.7

tabulated in table 3. These interaction virial coefficients can be fitted to a Lennard-Jones 6:12 potential model. The intermolecular force constants for the interaction between a nitrogen molecule and an oxygen molecule thus computed are:

$$\epsilon_0/k = 106.4^\circ$$

$$b = 61.1 \text{ cm}^3/\text{mole}$$

$$d = 3.64 \text{ \AA.}$$

The intermolecular potential energy is plotted as a function of the separation of the centers of the nitro-

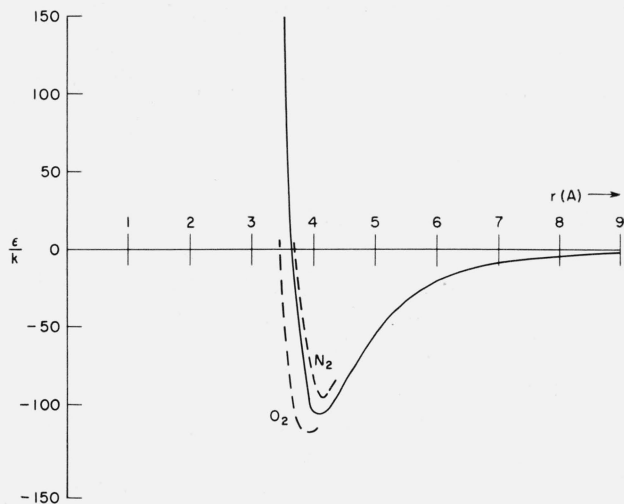


FIGURE 1. *Intermolecular potential between a nitrogen molecule and an oxygen molecule (solid line).*

The potential energy curves for oxygen-oxygen interactions and for nitrogen-nitrogen interactions are indicated by the dashed lines.

gen from the oxygen molecules in figure 1. The equation for this curve is

$$\frac{\epsilon}{k} = 4 \left(\frac{\epsilon_0}{k} \right) \left[\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 \right] \quad (7)$$

OR

$$\frac{\epsilon}{k} = 425.6 \left[(3.64/r)^{12} - (3.64/r)^6 \right]. \quad (8)$$

The collision diameter at the maximum energy of binding between the pair of interacting molecules

is $r_0 = d\sqrt{2}$. For nitrogen: oxygen collisions, $r_0 = 4.08 \text{ \AA.}$

- [1] A. S. Friedman, D. A. Gregory, R. Lindsay, and D. White (in preparation).
- [2] D. White, A. S. Friedman, and H. L. Johnston, *Phys. Rev.* **79**, 235, U11 (1950).
- [3] A. S. Friedman (Dissertation, Ohio State Univ., 1950).
- [4] D. White, A. S. Friedman, and H. L. Johnston, *Phys. Rev.* **79**, 235, U10 (1950).
- [5] L. Holborn and J. Otto, *Z. Physik* **10**, 367 (1922).
- [6] J. Hilsenrath et al., NBS Circular 564 (1955).

WASHINGTON, September 10, 1956.