

# Virial Coefficients and Models of Molecules in Gases\*

TARO KIHARA

*Department of Physics, University of Tokyo, Tokyo, Japan*

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## GENERAL INTRODUCTION

THE equation of state of gases may be expressed in the form

$$pv = kT(1 + Bv^{-1} + Cv^{-2} + \dots),$$

where  $p$  is the pressure,  $v$  is the volume per molecule,  $k$  is the Boltzmann constant, and  $T$  is the (absolute) temperature. In this expression  $B$ ,  $C$ ,  $\dots$ , which are functions of the temperature, are called the second, third,  $\dots$  virial coefficients. These coefficients indicate the deviation of a real equation of state from that of the ideal gas. It is a great success of statistical physics that these virial coefficients have been given in terms of the interaction between molecules, or the intermolecular potential. In fact, each virial coefficient is represented as an integral of a function of the intermolecular potential.

Besides the equation of state, the viscosity, isotopic thermal diffusion, and other transport properties of a gas are also intimately related to the intermolecular potential. In fact, each one of these properties is expressed in terms of effective cross sections for molecular collisions, which are also determined by the intermolecular potential.

The objective of the present article is to collect information about intermolecular potentials obtained from these properties of gases, particularly that by Japanese workers in recent years. In order to make the limits of our problem clear, we confine ourselves to pure, nonpolar, nonquantum gases.

For our purpose it is advisable to use suitable models of molecules. A suitable model must have both of the following two merits: (1) The model approximates

real molecules (accuracy). (2) Necessary integrals can be evaluated for the model (integrability).

A molecular theory of matter is usually based upon the assumption that the total potential energy is equal to the sum of the potential energies between pairs of molecules. We also have to assume this additivity of the intermolecular potential.

## I. THE SECOND AND THE THIRD VIRIAL COEFFICIENTS FOR SPHERICAL MOLECULES

### 1. Introduction

For spherically symmetric molecules, such as the rare gases, the potential energy between molecules,  $U$ , is a function only of the distance between the centers of molecules,  $r$ . In terms of  $r_{ij}$ , the distance between two molecules  $i$  and  $j$ , and by means of a function

$$f(r) = \exp[-U(r)/kT] - 1, \quad (1.1)$$

the expressions for the second and the third virial coefficients, derived from statistical mechanics,<sup>1</sup> are

$$B = -\frac{1}{2} \int f(r_{12}) d\tau_1 = -2\pi \int_0^\infty f(r)r^2 dr, \quad (1.2)$$

$$C = -\frac{1}{3} \int \int f(r_{12})f(r_{13})f(r_{23}) d\tau_1 d\tau_2, \quad (1.3)$$

where

$$d\tau_i \equiv dx_i dy_i dz_i,$$

( $x_i, y_i, z_i$ ) being the position of the molecule  $i$ .

There is a temperature,  $T_B$ , such that

$$B(T) > 0 \quad \text{for } T > T_B,$$

$$B(T) < 0 \quad \text{for } T < T_B.$$

The  $T_B$  is called the Boyle temperature, because Boyle's law holds better for this temperature than for other temperatures. Relative to the Boyle temperature, let us define a volume  $v_B$  by

$$v_B = \left( T \frac{dB}{dT} \right)_{T=T_B}.$$

It may be suitable to call this  $v_B$  van der Waals' molecular volume, since it is equal to the term concerned with molecular volume in van der Waals'

\* This work was carried out at the University of Wisconsin U. S. Naval Research Laboratory, Madison, Wisconsin.

<sup>1</sup>J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940).

TABLE I. Boyle temperature  $T_B$  and van der Waals volume  $v_B$  for the rare gases.

	$T_B^\circ\text{K}$	$v_B \text{ \AA}^3$
Ne	123	35.5
A	410	67.4
Kr	594	78.5
Xe	772	114

equation of state. The values of  $T_B$  and  $v_B$  for the rare gases are given in Table I.

Taking the characteristic values  $T_B$  and  $v_B$  as units, let us consider dimensionless "reduced virial coefficients"

$$B^*\left(\frac{T}{T_B}\right) = \frac{B(T)}{v_B}, \quad C^*\left(\frac{T}{T_B}\right) = \frac{C(T)}{v_B^2},$$

in which  $B^*$  is normalized as

$$B^*(1) = 0, \quad [dB^*(t)/dt]_{t=1} = 1.$$

The  $B^*$  and  $C^*$  for the rare gases, which have been obtained from observed values given in Table II, are shown in Figs. 2 and 5 in the following two sections.

TABLE II. Second and third virial coefficients for the rare gases.

	$T^\circ\text{K}$	$B \text{ \AA}^3$	$C \times 10^{-3} \text{ \AA}^6$	Reference
Ne	65.2	-34.8	15.5	a
	90.6	-13.6	12.2	
	123	0.2	6.1	
	173	10.7	5.5	
	223	15.1	6.3	
	273	17.7	7.0	
	373	19.7	...	
	473	21.7	...	
	573	22.8	...	
	673	22.8	...	
A	173	-106.8	...	a
	223	-62.7	48	
	273	-36.7	46	
	323	-18.3	33	
	373	-7.1	31	
	423	1.9	27	
	473	7.8	27	
	573	18.6	...	
Kr	273	-104.5	76	b
	323	-71.1	62	
	373	-47.9	54	
	423	-31.2	48	
	473	-18.5	44	
	523	-9.5	45	
	573	-1.9	44	
Xe	290	-229	175	c
	323	-184	146	
	373	-135	113	
	423	-100.9	96	
	473	-75.4	84	
	523	-55.2	74	
	573	-39.1	67	

<sup>a</sup> L. Holborn and J. Otto, Z. Physik, **33**, 1 (1925).

<sup>b</sup> Beattie, Brierley, and Barriault, J. Chem. Phys. **20**, 1615 (1952).

<sup>c</sup> Beattie, Barriault, and Brierley, J. Chem. Phys. **19**, 1222 (1951).

## 2. Square-Well Potential<sup>2</sup>

The simplest model for which both the second and the third virial coefficients have been calculated is that of the square-well potential:

$$U(r) = \begin{cases} \infty & \text{for } r < \sigma \\ -\epsilon & \text{for } \sigma < r < g\sigma \\ 0 & \text{for } g\sigma < r \end{cases} \quad (2.1)$$

(Fig. 1). Here  $\sigma$  means the collision radius between molecules or, in our case of one-component gases, the diameter of a molecule.

Substituting (2.1) into (1.1), we have

$$f(r) = \begin{cases} -1 & \text{for } r < \sigma \\ x & \text{for } \sigma < r < g\sigma \\ 0 & \text{for } g\sigma < r, \end{cases}$$

where

$$x = \exp(\epsilon/kT) - 1. \quad (2.2)$$

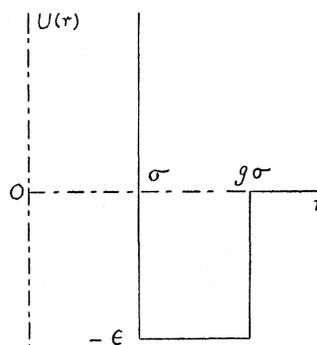


Fig. 1. Square-well potential.

The second virial coefficient (1.2) is expressed as a linear function of this  $x$ :

$$B = 4v_0[1 - (g^3 - 1)x], \quad (2.3)$$

in which

$$v_0 \equiv \frac{\pi}{6}\sigma^3$$

is the volume of the molecule.

Relations between  $T_B$  and  $\epsilon$  and between  $v_B$  and  $v_0$  are calculated to be

$$\frac{\epsilon}{kT_B} = \ln \frac{g^3}{g^3 - 1}, \quad (2.4)$$

$$\frac{v_B}{4v_0} = g^3 \ln \frac{g^3}{g^3 - 1}. \quad (2.5)$$

The third virial coefficient can be expressed as a cubic function of  $x$ ;

$$3C = I^{(0)} - 3xI^{(1)} + 3x^2I^{(2)} - x^3I^{(3)}. \quad (2.6)$$

<sup>2</sup> T. Kihara, Nippon Sugaku-Buturigakukai **17**, 11 (1943).

Here  $I^{(i)}$  are values of  $\int \int d\tau_1 d\tau_2$  integrated over the following regions.

- $I^{(0)}$ :  $r_{12} < \sigma, r_{13} < \sigma, r_{23} < \sigma$ ;
- $I^{(1)}$ :  $\sigma < r_{12} < g\sigma, r_{13} < \sigma, r_{23} < \sigma$ ;
- $I^{(2)}$ :  $\sigma < r_{12} < g\sigma, \sigma < r_{13} < g\sigma, r_{23} < \sigma$ ;
- $I^{(3)}$ :  $\sigma < r_{12} < g\sigma, \sigma < r_{13} < g\sigma, \sigma < r_{23} < g\sigma$ .

Let  $W(a, b, c)$  generally be the value of  $\int \int d\tau_1 d\tau_2$  integrated over the region

$$r_{12} < a, r_{13} < b, r_{23} < c.$$

Since  $W$  is symmetric with respect to  $a, b, c$ , it is sufficient to calculate it in the case  $a \geq b, a \geq c$ . It is clear that  $W$  is given by

$$W(a, b, c) = 4\pi \int_0^c V(a, b, r) r^2 dr,$$

in which  $V(a, b, c)$  means the volume of the overlapping part of two spheres of radii  $a$  and  $b$  having a distance  $r$  between centers:

$$V(a, b, r) = (\pi/12)[r^3 - 6r(a^2 + b^2) + 8(a^3 + b^3) - 3(a^2 - b^2)^2 r^{-1}]$$

when  $a - b \leq r \leq a + b$ ,

$$= (4\pi/3)b^3$$

when  $r \leq a - b$ .

We obtain, therefore,

$$W(a, b, c) = (\pi^2/18)[a^6 + b^6 + c^6 + 18a^2b^2c^2 + 16(b^3c^3 + c^3a^3 + a^3b^3) - 9\{a^4(b^2 + c^2) + b^4(c^2 + a^2) + c^4(a^2 + b^2)\}]$$

when  $a \leq b + c$ ,

$$= (16\pi^2/9)b^3c^3$$

when  $a \geq b + c$ .

In terms of this function,  $I^{(i)}$  in (2.6) are given by

- $I^{(0)} = W(\sigma, \sigma, \sigma)$ ,
- $I^{(1)} = W(g\sigma, \sigma, \sigma) - I^{(0)}$ ,
- $I^{(2)} = W(g\sigma, g\sigma, \sigma) - I^{(0)} - 2I^{(1)}$ ,
- $I^{(3)} = W(g\sigma, g\sigma, g\sigma) - I^{(0)} - 3I^{(1)} - 3I^{(2)}$ .

Thus we obtain finally

$$C = 2v_0^2[5 - (g^6 - 18g^4 + 32g^3 - 15)x + (-2g^6 + 36g^4 - 32g^3 - 18g^2 + 16)x^2 - (6g^6 - 18g^4 + 18g^2 - 6)x^3] \text{ for } g \leq 2,$$

$$= 2v_0^2[5 - 17x + (32g^3 - 18g^2 - 48)x^2 - (5g^6 - 32g^3 + 18g^2 + 26)x^3] \text{ for } g \geq 2.$$

For example

$$C = 2v_0^2(5 - 17x + 136x^2 - 162x^3) \text{ for } g = 2.$$

Figure 2 shows these virial coefficients in the reduced forms. From Fig. 2 and consulting Fig. 3, we see the following facts:

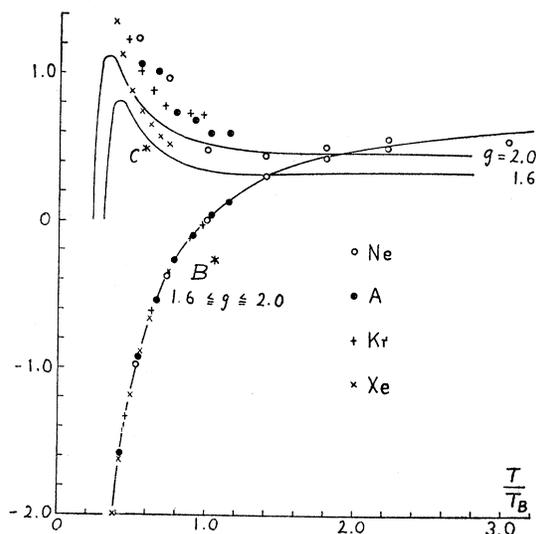


FIG. 2. Reduced virial coefficients compared with curves for the square-well potential.

1. The third virial coefficient  $C^*$  is sensitive to the shape of the potential, whereas the second virial coefficient  $B^*$  is insensitive to it.

2. If the bowl of the assumed potential is not sufficiently wide, the calculated  $C^*$  is too small.

3. The adequate value of  $g$  for the rare gases is about 2.0.

### 3. Lennard-Jones Potential

Assuming that

$$U(r) = \frac{\lambda}{r^n} - \frac{\mu}{r^m} = U_0 \left[ \frac{m}{n-m} \left(\frac{r_0}{r}\right)^n - \frac{n}{n-m} \left(\frac{r_0}{r}\right)^m \right], \quad (3.1)$$

$$\lambda, \mu > 0, \quad n > m > 3,$$

Lennard-Jones<sup>3</sup> evaluated the second virial coefficient (1.2) in the form of a power series. Integrating by parts,

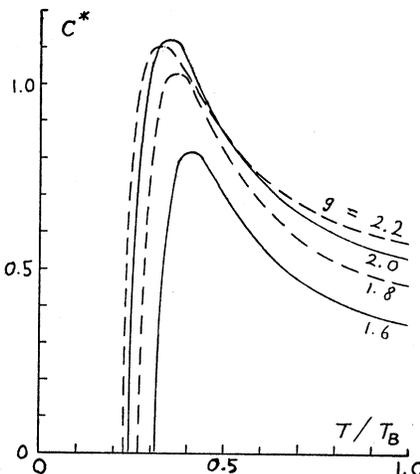


FIG. 3. Reduced third virial coefficient calculated for the square-well potential.

<sup>3</sup> Lennard-Jones, Proc. Roy. Soc. (London) A106, 463 (1924), Proc. Phys. Soc. (London) A43, 461 (1931).

he first obtained from (1.2)

$$B = -\frac{2\pi}{3} \int_0^\infty \frac{1}{kT} \frac{dU(r)}{dr} \exp\left[-\frac{U(r)}{kT}\right] r^3 dr.$$

Expanding  $\exp(\mu/r^m kT)$  of  $\exp[-U(r)/kT]$  into a power series and integrating term by term, he obtained

$$B = -\frac{2\pi}{n} \left(\frac{\lambda}{kT}\right)^{3/n} \sum_{t=0}^{\infty} \Gamma\left(\frac{tm-3}{n}\right) \frac{y^t}{t!}, \quad (3.2)$$

$$y \equiv \frac{\mu}{kT} \left(\frac{kT}{\lambda}\right)^{m/n}.$$

Two neutral nonpolar molecules at a sufficiently large distance apart attract each other with a potential inversely proportional to the sixth power of the distance. It is reasonable, therefore, to choose  $m=6$ .

The expression (3.2) can be transformed into

$$B = \frac{2\pi}{3} r_0^3 F_3\left(\frac{U_0}{kT}\right), \quad (3.3)$$

where

$$F_3(z) = -\frac{3}{n} \sum_{t=0}^{\infty} \frac{1}{t!} \Gamma\left(\frac{tm-3}{n}\right) \left(\frac{n}{m}\right)^t \left(\frac{m}{n-m}\right)^{[(n-m)t+3]/n} z^t.$$

(The suffix 3 indicates that this function is one of the  $F_s$  in section 9. In the case  $m=6$ ,  $n=12$ , the  $F_s$  are given in Table X.) In the case  $m=6$ , the Boyle temperature,  $T_B$ , and the van der Waals volume,  $v_B$ , are related to the model constants as follows:

$$\begin{aligned} kT_B &= 4.57U_0, & v_B &= 1.00r_0^3 & \text{for } n=9; \\ kT_B &= 3.44U_0, & v_B &= 1.20r_0^3 & \text{for } n=12; \\ kT_B &= 1.17U_0, & v_B &= 2.46r_0^3 & \text{for } n=\infty. \end{aligned}$$

The series expansion technique can also be applied to the third virial coefficient.<sup>4</sup> Let us transform the integration variables of (1.3) as follows:

$$\begin{aligned} C &= -\frac{1}{3} \int \int f(r_{12})f(r_{13})f(r_{23})d\tau_1d\tau_2 \\ &= -\int \int_{r_{12}>r_{13}, r_{12}>r_{23}} f(r_{12})f(r_{13})f(r_{23})d\tau_1d\tau_2 \\ &= -4\pi^2 \int_0^{\frac{1}{2}} \int_{1-(1-y^2)^{\frac{1}{2}}}^{(1-y^2)^{\frac{1}{2}}} \int_0^\infty f(r_{12})f(r_{13})f(r_{23}) \\ &\quad \times R^5 dR dx dy^2, \quad (3.4) \end{aligned}$$

where (see Fig. 4)

$$R = r_{12}, \quad (x^2 + y^2)R^2 = r_{13}^2, \quad [(1-x)^2 + y^2]R^2 = r_{23}^2.$$

<sup>4</sup> T. Kihara, J. Phys. Soc. Japan, 3, 265 (1948); 6, 184 (1951).

First we carry out the integration with respect to  $R$ . Integrating by parts we have

$$\begin{aligned} & -\int_0^\infty f(r_{12})f(r_{13})f(r_{23})R^5 dR \\ &= \frac{1}{6} \int_0^\infty \frac{\partial f(r_{12})f(r_{13})f(r_{23})}{\partial R} R^6 dR. \quad (3.5) \end{aligned}$$

Here the product of  $f$  functions can be written as the sum

$$\begin{aligned} f(r_{12})f(r_{13})f(r_{23}) &= f^{(0)} - f^{(1)} - f^{(2)} - f^{(3)} \\ &\quad + f(r_{12}) + f(r_{13}) + f(r_{23}), \end{aligned}$$

in which

$$\begin{aligned} f^{(0)} &= \exp[-(kT)^{-1}\{U(r_{12})+U(r_{13})+U(r_{23})\}] - 1, \\ f^{(1)} &= \exp[-(kT)^{-1}\{U(r_{12})+U(r_{13})\}] - 1, \\ f^{(2)} &= \exp[-(kT)^{-1}\{U(r_{12})+U(r_{23})\}] - 1, \\ f^{(3)} &= \exp[-(kT)^{-1}\{U(r_{13})+U(r_{23})\}] - 1. \end{aligned}$$

For  $m>6$ , the integral of the sum of these seven terms can be evaluated by the sum of the seven integrals,

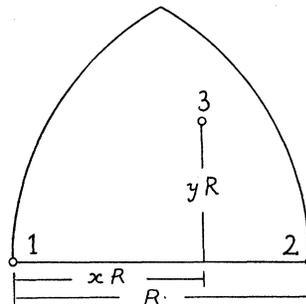


FIG. 4. The  $(x, y)$  domain of integration for (3.4).

each integral concerning each term. Therefore, in the same way as that of Lennard-Jones, we can expand (3.5) into

$$\begin{aligned} & -\frac{1}{n} \left(\frac{\lambda}{kT}\right)^{6/n} \sum_{t=0}^{\infty} C_t y^t, \\ & y = \frac{\mu}{kT} \left(\frac{kT}{\lambda}\right)^{m/n}, \end{aligned}$$

where

$$\begin{aligned} C_t &= \frac{1}{t!} \Gamma\left(\frac{tm-6}{n}\right) \left[ (1+\xi^n+\eta^n)^{6/n} \left\{ \frac{1+\xi^m+\eta^m}{(1+\xi^n+\eta^n)^{m/n}} \right\}^t \right. \\ &\quad - (1+\xi^n)^{6/n} \left\{ \frac{1+\xi^m}{(1+\xi^n)^{m/n}} \right\}^t \\ &\quad - (1+\eta^n)^{6/n} \left\{ \frac{1+\eta^m}{(1+\eta^n)^{m/n}} \right\}^t \\ &\quad \left. - (\xi^n+\eta^n)^{6/n} \left\{ \frac{\xi^m+\eta^m}{(\xi^n+\eta^n)^{m/n}} \right\}^t + 1 + \xi^6 + \eta^6 \right], \\ \xi &= R/r_{13} = (x^2+y^2)^{-\frac{1}{2}}, \quad \eta = R/r_{23} = [(1-x)^2+y^2]^{-\frac{1}{2}}. \end{aligned}$$

Thus we obtain

$$C = -\frac{4\pi^2}{n} \left(\frac{\lambda}{kT}\right)^{6/n} \sum_{t=0}^{\infty} y^t \int_0^{\frac{1}{2}} \int_{1-(1-y^2)^{\frac{1}{2}}}^{(1-y^2)^{\frac{1}{2}}} C_t dx dy (y^2). \quad (3.6)$$

In the case we need,  $m=6$ ,  $C_1$  becomes indefinite. We may, however, take the limit  $m \rightarrow 6$ , since in the original form this value is not any singular point:

$$\lim_{m \rightarrow 6} C_1 = \ln \frac{(1+\xi^n)(1+\eta^n)}{1+\xi^n+\eta^n} + \xi^6 \ln \frac{(1+\xi^n)(\xi^n+\eta^n)}{\xi^n(1+\xi^n+\eta^n)} + \eta^6 \ln \frac{(1+\eta^n)(\xi^n+\eta^n)}{\eta^n(1+\xi^n+\eta^n)}.$$

Let us fix  $m$  equal to 6, and confine ourselves to the  $(6, n)$  potential

$$U(r) = U_0 \left[ \frac{6}{n-6} \left(\frac{r_0}{r}\right)^n - \frac{n}{n-6} \left(\frac{r_0}{r}\right)^6 \right] \quad (3.7)$$

hereafter.

TABLE III. Coefficients in the series expansion (3.8) of the third virial coefficient for Lennard-Jones (6.9) and (6.12) potentials.

$t$	$\gamma_t(9)$	$\gamma_t(12)$
0	+1.561	+1.383
1	-2.940	-2.562
2	+0.929	+1.215
3	0.716	0.766
4	0.503	0.343
5	0.291	0.047
6	0.105	-0.112
7	-0.04	-0.168
8	-0.14	-0.164
9	-0.20	-0.134
10	-0.23	-0.098
11	-0.23	-0.067

Our result (3.6) may be written as

$$C = 10v_0^3 \sum_{t=0}^{\infty} \gamma_t(n) \left(\frac{y}{2}\right)^t, \quad (3.8)$$

where

$$v_0 = \frac{\pi}{6} \left(\frac{\lambda}{kT}\right)^{3/n} = \frac{\pi}{6} r_0^3 \left(\frac{6}{n-6} \frac{U_0}{kT}\right)^{3/n},$$

$$\frac{y}{2} = \frac{1}{2} \frac{\mu}{kT} \left(\frac{kT}{\lambda}\right)^{6/n} = \frac{n}{12} \left(\frac{6}{n-6} \frac{U_0}{kT}\right)^{(n-6)/n}.$$

The values of  $\gamma_t(n)$ , which have been obtained by numerical calculation of the double integrals, are given in Table III.<sup>5</sup>

Comparison with observed values is shown in Fig. 5. Consulting the conclusions of the preceding section, we see that the bowl of the Lennard-Jones (6, 12) po-

<sup>5</sup> In the case of (6, 12) potential, a highly accurate table for  $C$  is given by Bird, Spatz, and Hirschfelder, *J. Chem. Phys.* **18**, 1395 (1950).

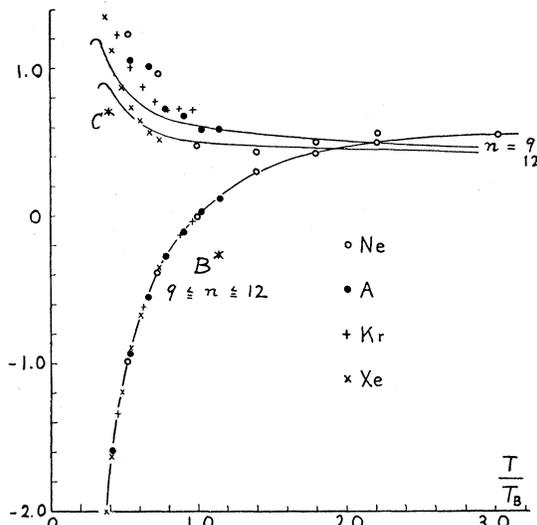


FIG. 5. Reduced virial coefficients compared with curves for Lennard-Jones (6,  $n$ ) potential.

tential is not sufficiently wide for molecules of the rare gases.

#### 4. Inverse-Power Repulsive Potential

When the attractive part of the intermolecular potential is negligible, the model

$$U(r) = \lambda r^{-n}, \quad \lambda > 0, \quad n > 3 \quad (4.1)$$

may be used. The exponent  $n$  may be seen as a measure of the hardness of the molecules.

In this case the  $(\nu+1)$ -th virial coefficient is written in the form  $b_\nu (\lambda/kT)^{3\nu/n}$ ,  $b_\nu$  being independent of the temperature. In particular, from (3.2), the second virial coefficient is

$$B = \frac{2\pi}{3} \Gamma\left(\frac{n-3}{n}\right) \left(\frac{\lambda}{kT}\right)^{3/n}, \quad (4.2)$$

and, from (3.8), the third virial coefficient is

$$C = \frac{5\pi^2}{18} \gamma_0(n) \left(\frac{\lambda}{kT}\right)^{6/n}. \quad (4.3)$$

The values of  $\gamma_0(n)$  are given in Table IV.

This inverse-power repulsive potential, and therefore the results (4.2) and (4.3), can be applied to gases at

TABLE IV. Numerical factor in the third virial coefficient (4.3) for the inverse  $n$ th power potential.

$n$	$\gamma_0(n)$
6	2.032
9	1.561
12	1.383
15	1.291
18	1.233
$\infty$	1.000

extremely high temperatures, such as gases produced by detonations.<sup>6</sup>

## II. CRITICISM OF THE LENNARD-JONES POTENTIAL

### 5. Transport Properties of Gases

In Sec. 3 we came near concluding that the bowl of the Lennard-Jones (6,  $n$ ) potential with  $n=12$  is too narrow for molecules of the rare gases. So long as we use the (6,  $n$ ) potential we will have to choose  $n < 12$  if we want a wider bowl. In reality, however, the state of affairs is not so simple since the choice of small  $n$  exerts some influence on properties of the gas at high temperatures.

Transport properties of a gas at moderate densities can be expressed in terms of effective cross sections  $\Omega^{(l)}(r)$  defined by<sup>7</sup>

$$\Omega^{(l)}(r) = \pi^{\frac{1}{2}} \int_0^{\infty} \phi^{(l)} V^{2r+2} \exp(-V^2) dV, \\ \phi^{(l)} = \int_0^{\infty} (1 - \cos^l \theta) g b db, \quad (5.1) \\ l=1, 2, \dots; \quad r=l, l+1, l+2, \dots.$$

TABLE V. Functions defined by (5.2) for (6,  $\infty$ ) potential (5.3),  $\zeta$  being given by (5.4).<sup>a</sup>

$\zeta$	$F_1^1(\zeta)$	$F_2^1(\zeta)$	$F_2^2(\zeta)$	$F_3^2(\zeta)$
0.00	0.5000	1.5000	1.0000	4.0000
0.01	0.5017	1.5034	1.0036	4.0106
0.02	0.5036	1.5068	1.0074	4.0218
0.03	0.5056	1.5102	1.0116	4.0335
0.04	0.5077	1.5137	1.0159	4.0457
0.05	0.5099	1.5173	1.0205	4.0585
0.075	0.5159	1.5268	1.0330	4.0927
0.100	0.5225	1.5369	1.0468	4.1299
0.125	0.5296	1.5478	1.0617	4.1700
0.150	0.5369	1.5595	1.0774	4.2127
0.175	0.5444	1.5719	1.0939	4.2578
0.200	0.5521	1.5849	1.1115	4.3053
0.250	0.5674	1.6126	1.1464	4.4055
0.375	0.6048	1.6872	1.2376	4.6777
0.500	0.6401	1.7648	1.3264	4.9615
0.625	0.6733	1.8426	1.4090	5.2403
0.750	0.7045	1.9189	1.4846	5.5053
0.875	0.7338	1.9929	1.5537	5.7530
1.000	0.7614	2.0635	1.6167	5.9828
1.125	0.7874	2.1308	1.6753	6.1963
1.250	0.8119	2.1945	1.7294	6.3950
1.375	0.8351	2.2551	1.7800	6.5809
1.500	0.8571	2.3125	1.8275	6.7556
1.625	0.8780	2.3673	1.8725	6.9205
1.750	0.8981	2.4197	1.9153	7.0771
1.875	0.9172	2.4698	1.9560	7.2262
2.000	0.9357	2.5183	1.9950	7.3689

<sup>a</sup> The values are taken from M. Kotani, Proc. Phys. Math. Soc. Japan **24**, 76 (1942).

<sup>6</sup> T. Kihara and T. Hikita, *Fourth Symposium on Combustion* (Williams & Wilkins Company, Baltimore, Maryland, 1953), p. 458.

<sup>7</sup> S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, 1939).

Here  $g$  is the relative velocity,  $b$  the impact parameter,  $\theta$  the deflection angle in the orbit of relative motion, and

$$V = (m^*/2kT)^{\frac{1}{2}} g, \quad m^* = \text{reduced mass.}$$

In particular, when the Lennard-Jones (6,  $n$ ) potential

$$U(r) = \lambda r^{-n} - \mu r^{-6}$$

is adopted, the  $\Omega^{(l)}(r)$  are given in the form

$$\Omega^{(l)}(r) = \left( \frac{2\pi kT}{m^*} \right)^{\frac{1}{2}} \left( \frac{\lambda}{2kT} \right)^{2/n} F_r^l(\zeta), \quad (5.2)$$

in which

$$\zeta = \frac{1}{2kT} \left( \frac{\mu^n}{\lambda^6} \right)^{1/(n-6)}.$$

The functions  $F_r^l(\zeta)$  have been calculated for (6,  $\infty$ ) potential,<sup>8</sup> i.e.,

$$U(r) = \begin{cases} -\mu r^{-6} & \text{for } r > a \\ \infty & \text{for } r < a, \end{cases} \quad (5.3)$$

$$\zeta = \frac{1}{2kT} \frac{\mu}{\lambda a^6}, \quad (5.4)$$

and for (6, 12) potential,<sup>9,10</sup> i.e.,

$$U(r) = \frac{\lambda}{r^{12}} - \frac{\mu}{r^6} = U_0 \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right], \quad (5.5)$$

$$\zeta = \frac{1}{2kT} \frac{\mu^2}{\lambda} = \frac{2U_0}{kT}. \quad (5.6)$$

The results are given in Tables V and VI.

The viscosity,  $\eta$ , of a pure gas is given by

$$\eta = \frac{5kT}{8\Omega^{(2)}(2)} \left[ 1 + \frac{3}{49} \left( \frac{\Omega^{(2)}(3)}{\Omega^{(2)}(2)} - \frac{7}{2} \right)^2 \right] \quad (5.7)$$

(compare Appendix). Figure 6 shows calculated curves and observed values of the reduced viscosity

$$\eta(mkT)^{-\frac{1}{2}} v_B^{\frac{2}{3}},$$

where  $m$  is the mass per molecule, and  $T_B$  and  $v_B$  are taken from Table I.

The isotopic thermal diffusion ratio  $k_T$  is given by (compare Appendix)

$$k_T = \frac{15}{8} \frac{n_1 n_2}{(n_1 + n_2)^2} \frac{m_1 - m_2}{m_1 + m_2} \frac{2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)}{\Omega^{(2)}(2)}, \quad (5.8)$$

where  $m_1/m_2$  is the ratio of the masses of the two kinds of molecules ( $m_1 > m_2$ ), and  $n_1/(n_1 + n_2)$  and  $n_2/(n_1 + n_2)$

<sup>8</sup> M. Kotani, Proc. Phys.-Math. Soc. Japan **24**, 76 (1942).

<sup>9</sup> T. Kihara and M. Kotani, Proc. Phys.-Math. Soc. Japan **25**, 602 (1953).

<sup>10</sup> Hirschfelder, Bird, and Spotz, J. Chem. Phys. **16**, 968 (1948); **17**, 1343 (1949).

TABLE VI. Functions defined by (5.2) for (6, 12) potential (5.5),  $\zeta$  being given by (5.6).<sup>a</sup>

$\zeta$	$F_1^1(\zeta)$	$F_2^1(\zeta)$	$F_2^2(\zeta)$	$F_3^2(\zeta)$
0.000	0.5063	1.4344	1.1564	4.433
0.025	0.4950	1.4073	1.1201	4.310
0.050	0.4912	1.3976	1.1070	4.264
0.075	0.4889	1.3909	1.0982	4.232
0.100	0.4873	1.3859	1.0916	4.207
0.150	0.4857	1.3789	1.0828	4.171
0.200	0.4853	1.3745	1.0779	4.146
0.250	0.4858	1.3720	1.0755	4.129
0.375	0.4897	1.3710	1.0779	4.111
0.500	0.4964	1.3756	1.0883	4.117
0.625	0.5050	1.3842	1.1046	4.141
0.750	0.5150	1.3960	1.1251	4.179
0.875	0.5259	1.4104	1.1486	4.228
1.000	0.5376	1.4270	1.1749	4.286
1.125	0.5499	1.4456	1.2028	4.353
1.250	0.5626	1.4657	1.2321	4.425
1.375	0.5756	1.4872	1.2622	4.503
1.500	0.5887	1.5099	1.2930	4.586
1.625	0.6019	1.5336	1.3240	4.672
1.750	0.6151	1.5581	1.3549	4.761
1.875	0.6283	1.5833	1.3857	4.852
2.000	0.6413	1.6092	1.4162	4.944

<sup>a</sup> The values are taken from T. Kihara and M. Kotani, Proc. Phys.-Math. Soc. Japan 25, 602 (1943).

are their mole fractions. The "reduced thermal diffusion ratio,"

$$k_T^* \equiv k_T \left[ \frac{n_1 n_2}{(n_1 + n_2)^2} \frac{m_1 - m_2}{m_1 + m_2} \right]^{-1} = \frac{15}{8} \frac{2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)}{\Omega^{(2)}(2)},$$

is shown in Fig. 7, together with Stier's<sup>11</sup> observations.

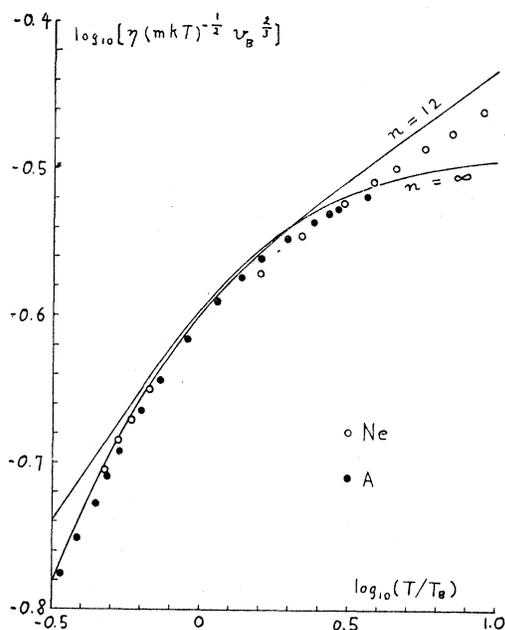


FIG. 6. Reduced viscosity compared with curves for Lennard-Jones (6,  $n$ ) potential.

<sup>11</sup> L. G. Stier, Phys. Rev. 62, 548 (1942).

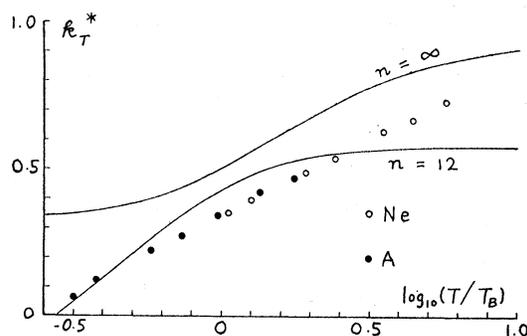


FIG. 7. Reduced thermal diffusion ratio compared with curves for Lennard-Jones (6,  $n$ ) potential.

From the discrepancies at high temperatures shown in Figs. 6 and 7, we may draw the following conclusion: In order to explain the transport properties of neon and argon (perhaps also krypton and xenon) at high temperatures it is necessary to choose  $n > 12$ . In other words, the repulsive wall of the intermolecular potential for rare gases is harder than that of the (6, 12) potential.

### Appendix to Section 5

The effective cross sections (5.1) depend, in general, on the temperature as

$$T \frac{d}{dT} \Omega^{(l)}(r) = \Omega^{(l)}(r+1) - (r + \frac{3}{2}) \Omega^{(l)}(r).$$

In particular, if  $\phi^{(l)}$  do not depend on the relative speed  $g$ ,  $\Omega^{(l)}(r)$  are independent of the temperature. Although the derivatives of  $\Omega^{(l)}(r)$  do not necessarily vanish for real molecules, the absolute values for

$$\frac{T^t}{\Omega^{(l)}(1)} \frac{d^t \Omega^{(l)}(1)}{dT^t}, \quad \frac{T^t}{\Omega^{(2)}(2)} \frac{d^t \Omega^{(2)}(2)}{dT^t}, \quad \dots, \quad t=1, 2, \dots$$

are always small.

The expression (5.7) for the viscosity is an approximation which has been obtained by neglecting derivatives of the second and higher orders and also neglecting third and higher powers of the first derivative. This approximation is simpler and more accurate, and therefore more convenient for numerical calculations, than Chapman and Cowling's<sup>7</sup> second approximation

$$\eta = \frac{5kT}{2\Omega^{(2)}(2)} \left( 1 + \frac{b_{12}^2}{b_{11}b_{22} - b_{12}^2} \right),$$

where

$$b_{11} = 4\Omega^{(2)}(2),$$

$$b_{12} = 7\Omega^{(2)}(2) - 2\Omega^{(2)}(3),$$

$$b_{22} = \frac{301}{12} \Omega^{(2)}(2) - 7\Omega^{(2)}(3) + \Omega^{(2)}(4).^{12}$$

<sup>12</sup> The accuracies of these two approximations are quantitatively compared by E. A. Mason, J. Chem. Phys. (to be published).

Similarly we obtain the thermal diffusion ratio for isotopes (5.8), which is simpler and, nevertheless, more accurate than Chapman and Cowling's first approximation,

$$k_T = \frac{n_1 n_2}{(n_1 + n_2)^2} \frac{m_1 - m_2}{m_1 + m_2} \times \frac{15[2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)][5\Omega^{(1)}(1) + \Omega^{(2)}(2)]}{\Omega^{(2)}(2)[55\Omega^{(1)}(1) - 20\Omega^{(1)}(2) + 4\Omega^{(1)}(3) + 8\Omega^{(2)}(2)]}.$$

As regards the thermal conductivity for monatomic gases, our approximation is

$$C_v \frac{25kT}{16\Omega^{(2)}(2)} \left[ 1 + \frac{2}{21} \left( \frac{\Omega^{(2)}(3)}{\Omega^{(2)}(2)} - \frac{7}{2} \right)^2 \right],$$

where  $C_v$  is the heat capacity at constant volume for the unit mass.

### 6. Stability of Crystal Structures

Before we draw our final conclusion, we want to examine another property of rare gases.

Neon, argon, krypton, and xenon crystallize at low temperatures in a lattice of *cubic* closest packing. For this lattice structure, the number of nearest neighbor molecules around one molecule is 12, the number of second nearest neighbors, which are  $2^{\frac{3}{2}}$  times farther away from the original molecule, is 6; and the third nearest neighbors are  $3^{\frac{3}{2}}$  times farther away. For hexagonal closest packing, on the other hand, the number of first nearest neighbors is also 12, that of the second nearest neighbors, which are  $2^{\frac{3}{2}}$  times farther away, is also 6; but the third nearest neighbors are  $(2 + \frac{2}{3})^{\frac{3}{2}}$  times farther away, a little nearer than the third nearest

neighbors in the cubic structure. In order to explain the stability of the cubic structure in comparison to the hexagonal one, we must therefore choose a potential with a more or less wide bowl, in so far as the additivity of the intermolecular potential is assumed.

Let us further assume, besides the assumption of the additivity, that the zero-point energy does not play any essential role regarding the stability of the cubic closest packing structure. (The solid helium seems to be hexagonal!) Then we can straightforwardly calculate the crystallization energies of these two lattice structures.<sup>13</sup> The comparison by means of the Lennard-Jones (6,  $n$ ) potential is shown in Fig. 8, from which it follows that the Lennard-Jones potential cannot explain the absolute stability of the cubic structure.

If we choose for another example

$$U(r) = U_0 \left[ \frac{6}{n-6} \exp \frac{n(r_0-r)}{r_0} - \frac{n}{n-6} \left( \frac{r_0}{r} \right)^6 \right], \quad (6.1)$$

the cubic structure can become more stable than the hexagonal structure for  $n < 8.675$  (see Fig. 8). Two Lennard-Jones potentials,  $n=9$ , and 12, and the potential (6.1) with the critical value  $n=8.675$  are compared in Fig. 9.

Thus we obtain the following result: In order to explain the stability of the cubic structure as compared to the hexagonal one, we have to choose a potential bowl wider than that of the Lennard-Jones (6, 12) potential in so far as the additivity of the intermolecular potential is assumed. This is in accordance with the conclusion reached in Sec. 3 which is also based on the assumption of additivity.

Of course the assumption of additivity for the potential is not strictly true. However, the result obtained on the basis of this assumption is more useful than a result based on the assumption of some arbitrary deviation from the additivity.

Now, consulting the result of Sec. 5, let us draw our final conclusion. *The real intermolecular potential for rare gases has a wider bowl and a harder repulsive wall than the Lennard-Jones (6, 12) potential.*

Although the Lennard-Jones potential cannot be considered as completely satisfactory, it is still highly valuable, since the value of a molecular model consists chiefly in its ability to be treated mathematically.

### III. THE SECOND VIRIAL COEFFICIENT FOR NONSPHERICAL MOLECULES

Having treated of monatomic gases, we investigate in this part the second virial coefficient of polyatomic molecules. Our way of proceeding is again to introduce a suitable model by use of which the second virial coefficient can be integrated analytically. The first two sections are preliminaries and our model of molecules will be introduced in the last section.

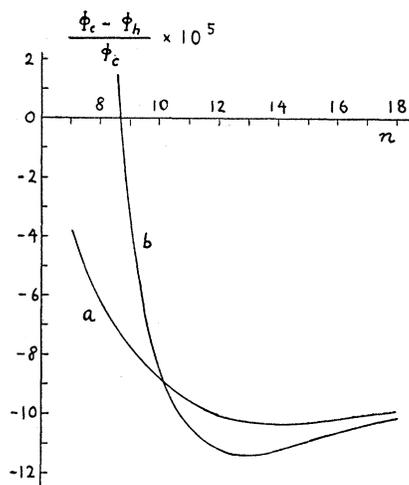


FIG. 8. Relative stability of the cubic closest packing structure to the hexagonal;  $\Phi_h/\Phi_c$  is the ratio of the crystallization energy of the hexagonal to the cubic. Curve "a" is for Lennard-Jones (6,  $n$ ) potential, curve "b" is for the potential (6.1).

<sup>13</sup> T. Kihara and S. Koba, J. Phys. Soc. Japan 7, 348 (1952).

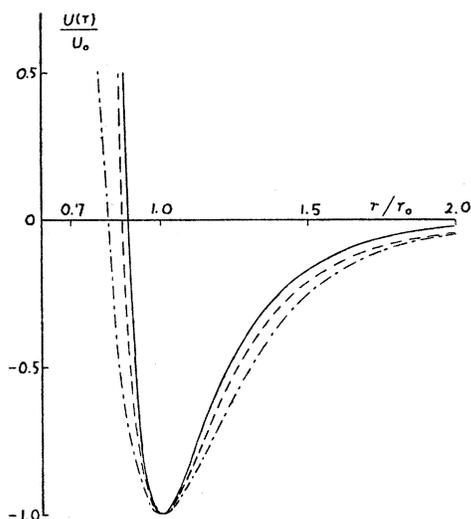


FIG. 9. Width of the bowl of intermolecular potentials. The full line is for Lennard-Jones (6, 12) potential, the broken line for Lennard-Jones (6, 9) potential, the chain line for the potential (6.1) with  $n=8.675$ .

7. Rigid Convex Body

A body is called convex if any line segment whose end points are inside lies entirely in that body.

Let us choose a coordinate origin  $O$  inside a (fixed) convex body and take coordinates of direction  $\theta$  and  $\varphi$  ( $0 \leq \theta \leq \pi$ ,  $0 \leq \varphi \leq 2\pi$ ). For any direction  $(\theta, \varphi)$ , there is one and only one plane which is in contact with the convex body and whose normal from the origin is in the direction  $(\theta, \varphi)$ . This plane is named the supporting plane in the direction  $(\theta, \varphi)$ ; the perpendicular distance from the origin to the supporting plane is called the supporting function, when it is considered as a function of  $\theta$  and  $\varphi$ . The supporting function will be denoted by  $H(\theta, \varphi)$ . Let us further denote by  $\langle H \rangle_{av}$  the average value of  $H(\theta, \varphi)$  with respect to all directions:

$$\langle H \rangle_{av} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi H(\theta, \varphi) \sin\theta d\theta d\varphi, \quad (7.1)$$

which is independent of the choice of the origin  $O$ .

Let us first assume that the convex body has a smooth surface and that each supporting plane has a contact of the first order with the convex body. Let  $\mathbf{r}(\theta, \varphi)$  be the radius vector from the origin to the contact point of the body with the supporting plane in the direction  $(\theta, \varphi)$ ; compare Fig. 10(a). Then the surface area  $S$  and the volume  $V$  of the convex body are given by

$$S = \int_0^{2\pi} \int_0^\pi \left| \frac{\partial \mathbf{r}}{\partial \theta} \times \frac{\partial \mathbf{r}}{\partial \varphi} \right| d\theta d\varphi \quad (7.2)$$

and

$$V = \frac{1}{3} \int_0^{2\pi} \int_0^\pi \mathbf{r} \cdot \left( \frac{\partial \mathbf{r}}{\partial \theta} \times \frac{\partial \mathbf{r}}{\partial \varphi} \right) d\theta d\varphi, \quad (7.3)$$

respectively.

Now we consider two convex bodies labelled  $A$  and  $B$  and in each body choose a coordinate origin  $O_A$  and  $O_B$ . The supporting function, the  $\mathbf{r}$  function, the volume, and the surface area will be denoted by

$$H_A(\theta, \varphi), \quad \mathbf{r}_A(\theta, \varphi), \quad V_A, \quad S_A,$$

and

$$H_B(\theta, \varphi), \quad \mathbf{r}_B(\theta, \varphi), \quad V_B, \quad S_B,$$

respectively. Keeping  $O_A$  and the orientation of  $A$  fixed, and keeping the orientation of  $B$  also fixed, let us move  $B$  around  $A$  keeping contact from outside. Then the locus of  $O_B$  forms the surface of another convex body, whose  $\mathbf{r}$  function is

$$\mathbf{r}(\theta, \varphi) = \mathbf{r}_A(\theta, \varphi) + \mathbf{r}_B^*(\theta, \varphi),$$

where

$$\mathbf{r}_B^*(\theta, \varphi) = -\mathbf{r}_B(\pi - \theta, -\varphi),$$

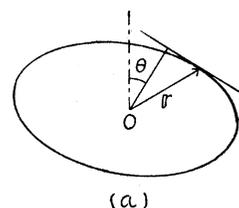
see Fig. 10(b). The volume of this third convex body,

$$V_{AB} = \frac{1}{3} \iint (\mathbf{r}_A + \mathbf{r}_B^*) \cdot \left[ \left( \frac{\partial \mathbf{r}_A}{\partial \theta} + \frac{\partial \mathbf{r}_B^*}{\partial \theta} \right) \times \left( \frac{\partial \mathbf{r}_A}{\partial \varphi} + \frac{\partial \mathbf{r}_B^*}{\partial \varphi} \right) \right] d\theta d\varphi,$$

must be first evaluated.

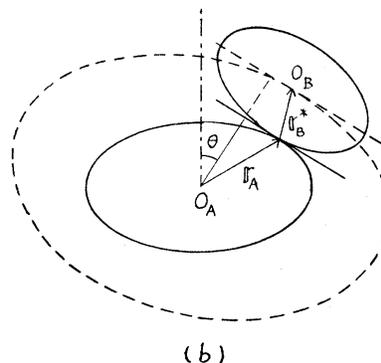
Considering the identity

$$\begin{aligned} & \frac{\partial}{\partial \theta} \left[ \mathbf{r}_B^* \cdot \left( \mathbf{r}_A \times \frac{\partial \mathbf{r}_A}{\partial \varphi} \right) \right] + \frac{\partial}{\partial \varphi} \left[ \mathbf{r}_B^* \cdot \left( \frac{\partial \mathbf{r}_A}{\partial \theta} \times \mathbf{r}_A \right) \right] \\ &= 2\mathbf{r}_B^* \cdot \left( \frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi} \right) - \mathbf{r}_A \cdot \left( \frac{\partial \mathbf{r}_B^*}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi} \right) \\ & \quad - \mathbf{r}_A \cdot \left( \frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_B^*}{\partial \varphi} \right), \end{aligned}$$



(a)

FIG. 10. Convex bodies and their supporting planes.



(b)

we have

$$\begin{aligned} \iint \left[ \mathbf{r}_A \cdot \left( \frac{\partial \mathbf{r}_B^*}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi} \right) + \mathbf{r}_A \cdot \left( \frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_B^*}{\partial \varphi} \right) \right] d\theta d\varphi \\ = 2 \iint \mathbf{r}_B^* \cdot \left( \frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi} \right) d\theta d\varphi, \end{aligned}$$

since the integral of the divergence expression vanishes. Making use of this relation and the other similar one, we obtain

$$\begin{aligned} V_{AB} = V_A + V_B + \iint \mathbf{r}_B^* \cdot \left( \frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi} \right) d\theta d\varphi \\ + \iint \mathbf{r}_A \cdot \left( \frac{\partial \mathbf{r}_B^*}{\partial \theta} \times \frac{\partial \mathbf{r}_B^*}{\partial \varphi} \right) d\theta d\varphi, \end{aligned}$$

or, in terms of the supporting functions

$$\begin{aligned} V_{AB} = V_A + V_B \\ + \iint H_B(\pi - \theta, \varphi) \left| \frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi} \right| d\theta d\varphi \\ + \iint H_A(\theta, \varphi) \left| \frac{\partial \mathbf{r}_B^*}{\partial \theta} \times \frac{\partial \mathbf{r}_B^*}{\partial \varphi} \right| d\theta d\varphi. \end{aligned}$$

Up to this point the orientation of the convex body  $B$  has been kept fixed. The next step is to take the average with respect to all orientations of the body  $B$ . When  $H_B$  in the third term on the right-hand side is averaged with respect to orientations of the body  $B$ , the value no longer depends on  $\theta$  and  $\varphi$  and is equal to  $\langle H_B \rangle_{Av}$ . The average value of the third term, therefore, is  $\langle H_B \rangle_{Av} S_A$ ; the fourth term is similarly  $\langle H_A \rangle_{Av} S_B$ . Hence the average value of  $V_{AB}$  becomes

$$\langle V_{AB} \rangle_{Av} = V_A + V_B + \langle H_B \rangle_{Av} S_A + \langle H_A \rangle_{Av} S_B. \quad (7.4)$$

After we have obtained this relation it is no longer necessary to assume that the convex body has a smooth surface and that each supporting plane has a contact of the first order with the convex body.

If the two convex bodies  $A$  and  $B$  are of the same shape, i.e., if  $V_A = V_B = V$ ,  $S_A = S_B = S$  and  $H_A = H_B = H$ , (7.4) becomes

$$2(V + \langle H \rangle_{Av} S). \quad (7.5)$$

The neat formula (7.4) or (7.5) was recently found by Ishihara;<sup>14</sup> the improved proof given above is partly due to Minkowski.<sup>15</sup>

For the evaluation of  $\langle H \rangle_{Av}$  the following theorem is useful:  $4\pi \langle H \rangle_{Av}$  is equal to the mean curvature inte-

grated over the whole surface of the convex body,

$$M \equiv \int \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) dS, \quad (7.6)$$

where  $R_1$  and  $R_2$  are the principal radii of curvature.<sup>16</sup> In terms of  $M$ , (7.5) becomes

$$2 \left( V + \frac{1}{4\pi} MS \right). \quad (7.7)$$

## 8. Parallel Bodies of a Convex Core

Definition: Let  $C$  be any convex body. A convex body formed by all points whose distances from  $C$  are smaller than or equal to  $\frac{1}{2}\rho$  is called the parallel body of  $C$  in the distance  $\frac{1}{2}\rho$ . Let us call the original body  $C$  the core of the parallel bodies.

We first consider as the core a convex polyhedron. Let the length of each edge be  $l_1, l_2, \dots, l_N$  ( $N$  being the number of edges of the polyhedron) and the angle of the  $i$ th edge be  $\alpha_i$  ( $i=1, 2, \dots, N$ ).

A parallel body of this polyhedron in the distance  $\frac{1}{2}\rho$  is composed of several parts of a sphere of diameter  $\rho$ , several parts of a circular cylinder of diameter  $\rho$ , and several parts of a plane. The surface integral of the mean curvature,  $M$ , of this parallel body is therefore given by

$$\begin{aligned} M = \frac{2}{\rho} \times (\text{surface area of all spherical parts}) \\ + \frac{1}{\rho} \times (\text{surface area of all cylindrical parts}). \end{aligned}$$

Since the spherical parts, when they are gathered together, form a complete sphere, we have

$$\begin{aligned} M = \frac{2}{\rho} \times (\text{surface area of a sphere of diameter } \rho) \\ + \frac{1}{\rho} \times \sum_{i=1}^N (\pi - \alpha_i) l_i = 2\pi\rho + M_0. \quad (8.1) \end{aligned}$$

Here

$$M_0 = \frac{1}{2} \sum_{i=1}^N (\pi - \alpha_i) l_i \quad (8.2)$$

is the surface integral of the mean curvature for the core. Similarly, the surface area  $S$  of the parallel body is

$$S = \pi\rho^2 + M_0\rho + S_0, \quad (8.3)$$

where  $S_0$  is the surface area of the core; and the volume

<sup>14</sup> A. Ishihara, J. Chem. Phys. **18**, 1446 (1950); A. Ishihara and T. Hayashida, J. Phys. Soc. Japan **6**, 40 and 46 (1951); T. Kihara, J. Phys. Soc. Japan **8**, 686 (1953).

<sup>15</sup> H. Minkowski, Math. Ann. **57**, 447 (1903).

<sup>16</sup> As regards the proof, compare for example, T. Bonnesen and W. Fenchel, *Theorie der konvexen Koerper* (Ergebnisse der Mathematik und ihrer Grenzgebiete, Bd. 3, Heft 1, Julius Springer, Berlin, 1934).

$V$  is

$$V = \frac{\pi}{6}\rho^3 + \frac{1}{4}M_0\rho^2 + \frac{1}{2}S_0\rho + V_0, \quad (8.4)$$

$V_0$  being the volume of the core.

Although we have been considering a polyhedron as the core, (8.1), (8.3), and (8.4) hold for parallel bodies of any convex core, since any convex body can be represented as a limit of polyhedrons.

In particular, when the core is a perpendicular prism of height  $l$ , area of the base  $f$ , and circumference of the base  $c$ , we have

$$V_0 = fl, \quad S_0 = 2f + cl, \quad M_0 = \pi l + (\pi/2)c. \quad (8.5)$$

From (8.5), taking the appropriate limit, we obtain

$$V_0 = 0, \quad S_0 = 2f, \quad M_0 = (\pi/2)c, \quad (8.6)$$

TABLE VII. Volume  $V_0$  surface area  $S_0$  and surface integral of the mean curvature  $M_0$  of convex cores.

Core	$V_0$	$S_0$	$M_0$
Sphere (radius $a$ )	$3^{-1}4\pi a^3$	$4\pi a^2$	$4\pi a$
Rectangular parallelepiped (length of each edge $l_1, l_2, l_3$ )	$l_1 l_2 l_3$	$2(l_1 l_2 + l_1 l_3 + l_2 l_3)$	$\pi(l_1 + l_2 + l_3)$
Regular tetrahedron (length of one edge $l$ )	$6^{-1}2^{-3/2}l^3$	$3\sqrt{2}l^2$	$6l \tan^{-1}(2\sqrt{2})$
Regular octahedron (length of one edge $l$ )	$3^{-1}2^{3/2}l^3$	$3\sqrt{2}l^2$	$12l \cot^{-1}(2\sqrt{2})$
Circular cylinder (length $l$ , radius $a$ )	$\pi a^2 l$	$2\pi a(a+l)$	$\pi(\pi a + l)$
Circular disk (radius $a$ )	0	$2\pi a^2$	$\pi^2 a$
Rectangle (length of each side $l_1, l_2$ )	0	$2l_1 l_2$	$\pi(l_1 + l_2)$
Regular triangle (length of one side $l$ )	0	$2^{-1}3^{1/2}l^2$	$2^{-1}3\pi l$
Regular hexagon (length of one side $l$ )	0	$3\sqrt{3}l^2$	$3\pi l$
Thin rod (length $l$ )	0	0	$\pi l$

for a thin plate ( $l=0$ ), and

$$V_0 = 0, \quad S_0 = 0, \quad M_0 = \pi l, \quad (8.7)$$

for a thin rod ( $f=0, c=0$ ).

The values of  $V_0$ ,  $S_0$ , and  $M_0$  for several typical shapes are given in Table VII.

### 9. Core Model

We assume an appropriate convex core inside each molecule and define the intermolecular distance  $\rho$  as the shortest distance between two cores. The intermolecular potential  $U$  is assumed to be a function of  $\rho$  only,  $U = U(\rho)$ , for which  $U(0) = \infty$ .

In order to determine the core of a molecule, it is necessary to have information about the interatomic distances (and bond angles if any) of the molecule. We prepare, therefore, Table VIII. Consulting this table we fix our cores as in Table IX; The volume  $V_0$ ,

TABLE VIII. Interatomic distances.<sup>a</sup>

Molecule	Bond	Distance in Å
H <sub>2</sub>	H—H	0.74
N <sub>2</sub>	N—N	1.094
CO <sub>2</sub>	C—O	1.15
CH <sub>4</sub>	C—H	1.093
CF <sub>4</sub>	C—F	1.42
C <sub>2</sub> H <sub>4</sub>	C—C	1.33
	C—H	1.087
	(Angle H—C—H is $2 \tan^{-1}(2\sqrt{2}) = 109^\circ 30'$ .)	
C <sub>6</sub> H <sub>6</sub>	C—C	1.39
	C—H	1.08

<sup>a</sup> The values are taken from L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948), pp. 167–172 and p. 196.

the surface area  $S_0$ , and the surface integral of the mean curvature  $M_0$  of the core are also tabulated.

For spherically symmetrical molecules the second virial coefficient  $B$  can be written in the form

$$B = \int_{r=0}^{r=\infty} \left[ 1 - \exp\left(-\frac{U(r)}{kT}\right) \right] db_0(r),$$

where  $b_0(r)$  is the second virial coefficient for a rigid sphere with diameter  $r$ :  $b_0(r) = 2\pi r^3/3$ . Similarly, for our core model  $B$  is given by

$$B = \int_{\rho=0}^{\rho=\infty} \left[ 1 - \exp\left(-\frac{U(\rho)}{kT}\right) \right] db(\rho) + b(0). \quad (9.1)$$

In this expression  $b(\rho)$  is the second virial coefficient for the rigid parallel body of our molecular core in the distance  $\frac{1}{2}\rho$ .

By consulting the statistical mechanical procedure of deriving (1.2), it is clear that  $b(\rho)$  is equal to one-half of (7.7),

$$b(\rho) = V + \frac{1}{4\pi}MS,$$

TABLE IX. The cores of molecules.

Hydrogen H <sub>2</sub> : thin rod connecting 2 H's (length 0.74Å)	$V_0 = 0,$	$S_0 = 0,$	$M_0 = 2.32A.$
Nitrogen N <sub>2</sub> : thin rod connecting 2 N's (length 1.094Å)	$V_0 = 0,$	$S_0 = 0,$	$M_0 = 3.44A.$
Carbon dioxide CO <sub>2</sub> : thin rod connecting 2 O's (length 2.30Å)	$V_0 = 0,$	$S_0 = 0,$	$M_0 = 7.23A.$
Methane CH <sub>4</sub> : regular tetrahedron connecting 4 H's (length of one edge 1.785Å)	$V_0 = 0.670A^3,$	$S_0 = 5.52A^2,$	$M_0 = 10.23A.$
Carbon tetrafluoride CF <sub>4</sub> : regular tetrahedron connecting 4 F's (length of one edge 2.32Å)	$V_0 = 1.47A^3,$	$S_0 = 9.32A^2,$	$M_0 = 13.30A.$
Ethylene C <sub>2</sub> H <sub>4</sub> : rectangle connecting the mid-point of each C—H bond (length of each side 0.89Å and 1.95Å)	$V_0 = 0,$	$S_0 = 3.47A^2,$	$M_0 = 8.92A.$
Benzene C <sub>6</sub> H <sub>6</sub> : regular hexagon connecting the mid-point of each C—H bond (length of one side 1.93Å)	$V_0 = 0,$	$S_0 = 19.4A^2,$	$M_0 = 18.2A.$

where  $M$ ,  $S$ , and  $V$  are given by (8.1), (8.3), and (8.4), respectively. We have, therefore,

$$b(\rho) = \frac{2\pi}{3}\rho^3 + M_0\rho^2 + \left(S_0 + \frac{1}{4\pi}M_0^2\right)\rho + \left(V_0 + \frac{1}{4\pi}M_0S_0\right). \quad (9.2)$$

If we assume, furthermore, the Lennard-Jones function for  $U(\rho)$

$$U(\rho) = U_0 \left[ \frac{m}{n-m} \left(\frac{\rho_0}{\rho}\right)^n - \frac{n}{n-m} \left(\frac{\rho_0}{\rho}\right)^m \right], \quad n > m > 3,$$

we obtain

$$B = \frac{2\pi}{3}\rho_0^3 F_3\left(\frac{U_0}{kT}\right) + M_0\rho_0^2 F_2\left(\frac{U_0}{kT}\right) + \left(S_0 + \frac{1}{4\pi}M_0^2\right)\rho_0 F_1\left(\frac{U_0}{kT}\right) + \left(V_0 + \frac{1}{4\pi}M_0S_0\right), \quad (9.3)$$

TABLE X. Functions in the second virial coefficient (9.3) for the core model (9.4).<sup>a</sup>

$-\log_{10}z$	$F_3(z)$	$F_2(z)$	$F_1(z)$
-0.4	-9.859	-5.211	-1.784
-0.3	-6.138	-3.008	-0.7761
-0.2	-4.003	-1.776	-0.2221
-0.1	-2.673	-1.027	0.1091
0.0	-1.795	-0.5424	0.3198
0.1	-1.189	-0.2151	0.4600
0.2	-0.7587	0.0132	0.5562
0.3	-0.4465	0.1758	0.6234
0.4	-0.2170	0.2930	0.6710
0.5	-0.0469	0.3779	0.7045
0.6	0.0794	0.4392	0.7279
0.7	0.1729	0.4829	0.7436
0.8	0.2415	0.5134	0.7536
0.9	0.2911	0.5336	0.7591
1.0	0.3259	0.5459	0.7611
1.1	0.3493	0.5521	0.7603
1.2	0.3638	0.5534	0.7575
1.3	0.3715	0.5510	0.7528
1.4	0.3737	0.5457	0.7468
1.5	0.3718	0.5381	0.7396
1.6	0.3668	0.5287	0.7320
1.7	0.3594	0.5179	0.7228
1.8	0.3501	0.5062	0.7135
1.9	0.3396	0.4937	0.7038
2.0	0.3281	0.4806	0.6937

<sup>a</sup> The values are taken from T. Kihara, *Nippon Buturigakukai* **2**, 11 (1947). The functions

$$F_s(z) = \frac{d}{dz}[zF_s(z)], \quad s=1, 2, 3,$$

which are necessary for investigation of the Joule-Thomson effect, are also tabulated in the same paper.

TABLE XI. The second virial coefficient for nonspherical molecules.

	$T^\circ\text{K}$	$B \text{ A}^3$	Reference		
H <sub>2</sub>	65.1	-30.3	a		
	90.0	-9.2			
	123	4.9			
	173	15.1			
	223	20.0			
	273	23.2			
	323	25.1			
	373	25.7			
	473	26.0			
	N <sub>2</sub>	143		-132	a
173		-86.0			
223		-43.8			
273		-17.2			
323		-0.4			
373		10.2			
423		19.1			
473		25.5			
573		34.3			
673		39.0			
CO <sub>2</sub>	273	-241	b		
	323	-170			
	373	-119			
	423	-84.0			
	473	-56.6			
	573	-22.5			
	673	-2.6			
	773	10.0			
	873	20.1			
	CH <sub>4</sub>	273		-89.6	c
298		-72.1			
323		-57.6			
348		-46.1			
373		-35.9			
398		-27.2			
423		-19.3			
CF <sub>4</sub>		273	-184	d	
		323	-117		
		373	-71.6		
	423	-43.2			
	523	-2.1			
	573	15.4			
	673	38.2			
C <sub>2</sub> H <sub>4</sub>	273	-280	e		
	298	-234			
	323	-197			
	348	-166			
	373	-142			
	398	-121			
423	-104				
C <sub>6</sub> H <sub>6</sub>	316	-2160	f		
	331	-1890			
	353	-1610			
	372	-1520			
	398	-1220			

<sup>a</sup> The data are due to Holborn and Otto; the values are taken from Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1939), p. 283.

<sup>b</sup> K. E. MacCormack and W. G. Schneider, *J. Chem. Phys.* **18**, 1269 (1950).

<sup>c</sup> A. Michels and G. W. Nederbragt, *Physica* **3**, 569 (1936).

<sup>d</sup> K. E. MacCormack and W. G. Schneider, *J. Chem. Phys.* **19**, 845, 849 (1951).

<sup>e</sup> A. Michels and M. Geldermans, *Physica* **9**, 967 (1942).

<sup>f</sup> Francis, McGlashan, Hamann, and McManamey, *J. Chem. Phys.* **20**, 1341 (1952).

where

$$F_s(z) = \int_0^\infty \left[ 1 - \exp\left(-\frac{m}{n-m} \frac{z}{\xi^n} + \frac{n}{n-m} \frac{z}{\xi^m}\right) \right] d(\xi^s)$$

$$= -\frac{s}{n} \sum_{t=0}^{\infty} \frac{1}{t!} \Gamma\left(\frac{tm-s}{n}\right) \times \left(\frac{n}{m}\right)^t \left(\frac{m}{n-m} z\right)^{[(n-m)t+s]/n}$$

For the case  $m=6$ ,  $n=12$ , namely

$$U(\rho) = U_0 \left[ \left(\frac{\rho_0}{\rho}\right)^{12} - 2\left(\frac{\rho_0}{\rho}\right)^6 \right], \quad (9.4)$$

the values of  $F_3(z)$ ,  $F_2(z)$ , and  $F_1(z)$  are given in Table X.

Making use of this table and observed values of the second virial coefficient given in Table XI, we can determine  $\rho_0$  and  $U_0/k$ ; the results are given in Table XII. Figure 11 shows the parallel body of the core in the

TABLE XII. The constants in the model (9.4) when the core is chosen as in Table IX.

	$\rho_0$ A	$U_0/k^\circ\text{K}$
H <sub>2</sub>	2.81	39.4
N <sub>2</sub>	3.47	124
CO <sub>2</sub>	3.36	309
CH <sub>4</sub>	1.92	378
CF <sub>4</sub>	2.48	372
C <sub>2</sub> H <sub>4</sub>	2.5	470
C <sub>6</sub> H <sub>6</sub>	3.4 <sup>a</sup>	830

<sup>a</sup> This value of  $\rho_0$  is taken from the lattice constant of graphite, since observed values for benzene are not sufficient to determine both  $\rho_0$  and  $U_0$ .

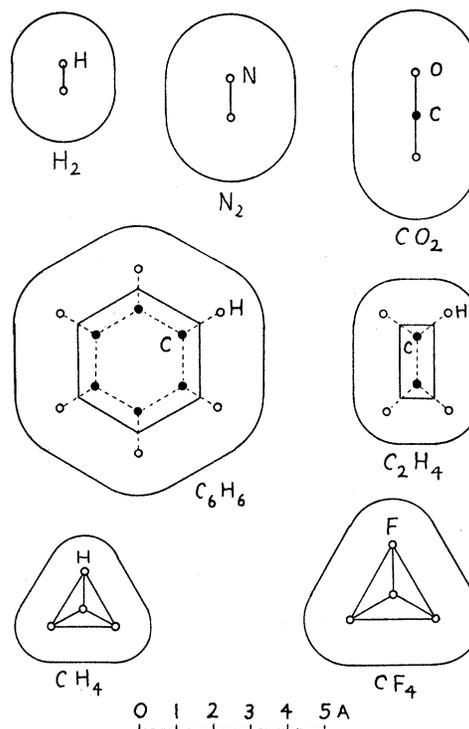


FIG. 11. Shape and size of molecules according to the core model.

distance of  $\frac{1}{2}\rho_0$ , which represents the shape and the size of each molecule.

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