

discussion of vacancy-impurity complexes in Sec. 3. From Eq. (3.15) and the above relation for ν_k , we find

$$\partial \ln \nu_k / \partial x = [\Delta h_2 + (1 - \rho)(h - E_{ij})](\nabla T / kT^2). \quad (A6)$$

When Eqs. (A3), (A5), and (A6) are substituted into Eq. (A1), we again find Eq. (3.16) with Q_k^* being given by Eq. (3.18) and D_k by Eqs. (A2) and (3.17), except that all factors of 7 are changed to 5.15 and the factor 13 is changed to 11.15. When it is assumed that $F_{ph} = 1$ for ω_3 jumps, even this difference between the final results obtained by the two methods disappears. The value of B in other cubic lattices can also be found from Eq. (A4). Equations for j_k and Soret gradient on these lattices are then found in the manner already described.

This method can also be used to obtain a purely atomistic derivation of \bar{v}_k without reference to Eq.

(5.1). This method gives¹²

$$\bar{v}_k = 2D_k \lambda^{-1} [A + B + \frac{1}{2} \lambda (\partial \ln f_k / \partial x)]. \quad (A7)$$

The quantity $(\partial \ln f_k / \partial x)$ can be found from Eq. (A2). When values of A and B from Eqs. (A3) and (A5) are substituted into Eq. (A7), we again find Eq. (5.4). Here Q_k^* is given by Eq. (3.18) and D_k by Eqs. (A2) and (3.17) if all factors of 7 are changed to 5.15 and the factor 13 is changed to 11.15. Expressions for \bar{v}_k in other cubic lattices can be found by evaluating Eq. (A4) for B in these lattices, and then proceeding as above. Equations (A2), (A3), and (A7) are valid for any cubic lattice.

ACKNOWLEDGMENT

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Second Virial Coefficient for the Spherical Shell Potential*

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Values of the second virial coefficient for the three-parameter spherical shell potential are tabulated over wide ranges of temperature and shell size. The potential, which is not new, results from the interaction of two spherical surfaces having uniform distributions of Lennard-Jones (6-12) sites.

An objective comparison is made between the tabulated values and the literature values for second virial coefficients, from which the potential parameters for twenty compounds are determined. Generally, the spherical shell potential generates a better fit than does the parent Lennard-Jones potential. The potential parameters found are in good agreement with expectations based upon density and interatomic distance data.

1. INTRODUCTION

TRADITIONALLY the equilibrium and transport properties of relatively small molecules have been correlated by the Lennard-Jones (6-12) potential. Other simpler potentials have also been employed, particularly when more extensive calculations were performed. A good discussion of these and more elaborate potentials can be found in Hirschfelder *et al.*¹ Recently the Morse² and Rydberg³ potentials have been investigated, and Bernades and Primakoff⁴ have presented

an interesting study involving a second-order contact between the Morse and Lennard-Jones potentials.

For larger molecules the Mie or Lennard-Jones potential apparently fails to correlate both equilibrium and transport properties with a single set of parameters, but in part the failure may be due to inadequacies in the existing transport theory as noted by Mason and Rice⁵ and others.⁶ The general success of the Mie⁷ potential for simpler systems, however, has prompted attempts to generalize the potential to larger systems. In particular, Thomaes⁸ and Atoji and Lipscomb⁹ have elaborated a spherical shell model related to the potential we have employed. The spherical shell model presumes Lennard-Jones interaction sites uniformly

* Based on a dissertation submitted in August, 1961, by William G. Hoover, in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The University of Michigan.

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¹ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *The Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

² D. D. Konowalow, M. H. Taylor, and J. O. Hirschfelder, *Phys. Fluids* **4**, 622 (1961).

³ O. Sinanoğlu and K. S. Pitzer, *J. Chem. Phys.* **31**, 960 (1959).

⁴ N. Bernades and H. Primakoff, *J. Chem. Phys.* **30**, 691 (1959).

⁵ E. A. Mason and W. E. Rice, *J. Chem. Phys.* **23**, 843 (1954).

⁶ A. G. De Rocco and J. O. Halford, *J. Chem. Phys.* **28**, 1152 (1958).

⁷ G. Mie, *Ann. Physik* **11**, 657 (1903).

⁸ G. Thomaes, *J. chim. phys.* **49**, 323 (1952).

⁹ M. Atoji and W. N. Lipscomb, *J. Chem. Phys.* **21**, 1480 (1953).

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¹⁰ S. D. Ham
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distributed over the surfaces of the interacting spheres. Hamann and Lambert¹⁰ have approximated the full potential by a 7-28 model, without marked improvement over the 6-12. In order to assess the value of the full spherical shell model we have examined in detail the experimental and calculated second virial coefficients for twenty compounds, half of which are spherical nonpolar substances, the rest being evenly divided between nonpolar, nonspherical molecules and polar molecules.

The spherical shell potential can be derived in the following fashion. In Fig. 1 the coordinate system is displayed, and it will be noticed that the indicated sites in I and II are separated by a distance l . Point P is first allowed to interact with all points on the surface of I, and is then moved over the full surface of II. The

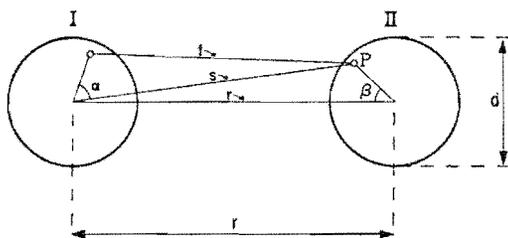


FIG. 1. Coordinates for calculation of the spherical shell potential.

potential of point P with respect to I is

$$\phi(P, d, s) = \frac{\int_0^{2\pi} d\theta \int_0^\pi t^{-N} (\frac{1}{2}d)^2 \sin\alpha d\alpha}{\int_0^{2\pi} d\theta \int_0^\pi (\frac{1}{2}d)^2 \sin\alpha d\alpha} \quad (1)$$

Using the law of cosines, $l^2 = (\frac{1}{2}d)^2 + s^2 - sd \cos\alpha$, we obtain

$$\phi(P, d, s) = \frac{1}{2} \int_0^\pi (s^2 + \frac{d^2}{4} - sd \cos\alpha)^{-(N-1)} \sin\alpha d\alpha, \quad (2)$$

and making the substitution, $\xi = l^2$ one arrives at

$$\phi(P, d, s) = \frac{1}{2sd} \int_{[s - (\frac{1}{2}d)]^2}^{[s + (\frac{1}{2}d)]^2} \xi^{-N} d\xi = \frac{sd}{(2-N)} \left[\frac{1}{[s + (\frac{1}{2}d)]^{2-N}} - \frac{1}{[s - (\frac{1}{2}d)]^{2-N}} \right]. \quad (3)$$

When Eq. (3) is expanded in inverse powers of s , it approaches s^{-N} as s grows large.

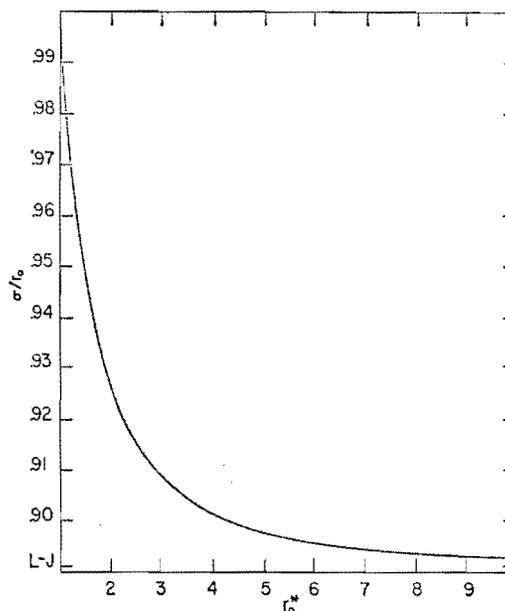


FIG. 2. Comparison of the characteristic distances σ (at which separation the potential energy is zero) and r_0 (at which separation the potential energy is a minimum) as a function of $r_0^* \equiv r_0/d$.

Integrating $\phi(P, d, s)$ over the surface of II yields

$$\phi(d, r) = \frac{1}{2} \int_0^\pi \phi(P, d, s) \sin\beta d\beta. \quad (4)$$

Noting that $s = [(\frac{1}{2}d)^2 + r^2 - rd \cos\beta]^{1/2}$, using $\phi(P, d, s)$ from Eq. (3) we obtain, finally,

$$\phi(r, d) = \frac{1}{rd^2(N-3)(N-2)} \times \left[\frac{1}{(r+d)^{N-3}} - \frac{2}{r^{N-3}} + \frac{1}{(r-d)^{N-3}} \right]. \quad (5)$$

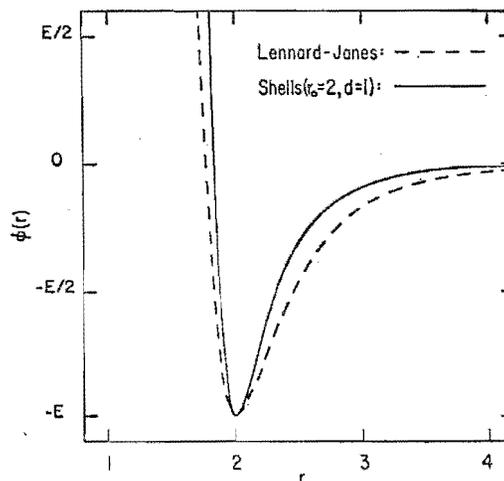


FIG. 3. Comparison of the Lennard-Jones and spherical shell potentials, using a common energy minimum.

¹⁰ S. D. Hamann and J. A. Lambert, Australian J. Chem. **7**, 1 (1954).

TABLE I. Potential parameters for spherical molecules (LJ values indicated by $r_0^* = \infty$).

Compound	r_0^*	$\epsilon/k(^{\circ}\text{K})$	$r_0(\text{Å})$	$d(\text{Å})$	σ^2	Reference
Carbon tetrafluoride (273 to 673°K)	1.70	322	4.55	2.68	3.7×10^{-4}	a
	∞	151	5.29	0.00	5.2×10^{-4}	
Cyclopropane (303 to 403°K)	1.70	635	4.41	2.60	7.5×10^{-6}	b
	∞	210	6.84	0.00	1.8×10^{-6}	
Krypton (273 to 573°K)	1.70	366	3.41	2.01	3.7×10^{-6}	c
	∞	172	4.00	0.00	1.5×10^{-4}	
Methane (273 to 423°K)	∞	147	4.30	0.00	3.0×10^{-6}	d
			(LJ potential gives better fit)			
Methane (108 to 249°K)	2.50	215	3.97	1.59	9.5×10^{-6}	e
	∞	123	4.95	0.00	3.2×10^{-4}	
Methane (108 to 423°K)	2.50	215	3.97	1.59	4.7×10^{-6}	d, e
	∞	145	4.43	0.00	4.2×10^{-4}	
Neopentane (434 to 548°K)	1.50	814	5.27	3.52	1.3×10^{-6}	f
	∞	259	7.65	0.00	8.6×10^{-6}	
Neopentane (300 to 548°K)	1.50	811	5.26	3.51	2.1×10^{-4}	f, g
	∞	230	8.49	0.00	4.7×10^{-4}	
Perfluorocyclobutane (373 to 623°K)	1.50	599	6.22	4.15	1.1×10^{-6}	h
	∞	222	7.92	0.00	7.4×10^{-6}	
Silicon tetrafluoride (293 to 353°K)	1.30	621	4.12	3.17	4.0×10^{-6}	i
	∞	148	6.31	0.00	8.8×10^{-6}	
Sulfur hexafluoride (293 to 448°K)	2.00	335	5.78	2.89	2.5×10^{-6}	j
	∞	186	6.72	0.00	2.7×10^{-6}	
Sulfur hexafluoride (273 to 523°K)	1.70	434	5.18	3.04	1.4×10^{-4}	k
	∞	196	6.35	0.00	2.3×10^{-4}	
Tetramethylsilane (323 to 403°K)	1.70	534	7.16	4.21	2.4×10^{-6}	l
	∞	209	9.80	0.00	5.9×10^{-6}	
Xenon (298 to 573°K)	3.00	292	4.30	1.43	3.2×10^{-6}	m
	∞	221	4.61	0.00	7.0×10^{-6}	

^a K. E. McCormack and W. G. Schneider, *J. Chem. Phys.* **19**, 849 (1951).

^b H. G. David, S. D. Hamann, and R. B. Thomas, *Australian J. Chem.* **12**, 309 (1959).

^c J. A. Beattie, J. S. Brierly, and R. J. Barriault, *J. Chem. Phys.* **20**, 1615 (1952).

^d H. W. Schamp, Jr., E. A. Mason, A. C. B. Richardson, and A. Altman, *Phys. Fluids* **1**, 329 (1958).

^e G. Thomaes and R. Van Steenwinkel, *Nature* **187**, 229 (1960).

^f J. A. Beattie, D. R. Douslin, and S. W. Levine, *J. Chem. Phys.* **20**, 1619 (1952).

^g H. M. Ashton and E. S. Halberstadt, *Proc. Roy. Soc. (London)* **A245**, 373 (1958); S. D. Hamann, J. A. Lambert, and R. B. Thomas, *Australian J. Chem.* **8**, 149 (1955).

^h D. R. Douslin, R. T. Moore, and G. Waddington, *J. Phys. Chem.* **63**, 1959 (1959).

ⁱ S. D. Hamann, W. J. McManamey, and J. F. Pearse, *Trans. Faraday Soc.* **49**, 351 (1953).

^j S. D. Hamann, J. A. Lambert, and R. B. Thomas, reference g, this table.

^k See reference a, this table.

^l S. D. Hamann, J. C. Lambert, and R. B. Thomas, reference g, this table.

^m Reference 1, p. 167.

We note that in the limit of large r , $\phi(r, d)$ becomes r^{-N} . In general, the expansion is a series of positive terms—the coefficients may be found in the paper of Atoji and Lipscomb⁹—and the first few for the case $N=6$ are displayed below:

$$\phi(r, d, N=6) = (6r^6)^{-1} [6 + 15(d/r)^2 + 28(d/r)^4 + 45(d/r)^6 + 66(d/r)^8 + \dots]. \quad (6)$$

This result was first obtained by Thomaes⁸ and later by Pitzer.¹¹ Combining the cases $N=6$ and $N=12$ from Eq. (5), we write

$$\phi(r, d) = (AP^{(9)}/r) - (BP^{(3)}/r), \quad (7)$$

¹¹ K. S. Pitzer, *J. Am. Chem. Soc.* **77**, 3427 (1955), incorrect beyond the second term.

where

$$P^{(N)} \equiv (r+d)^{-N} - 2r^{-N} + (r-d)^{-N}, \quad (8)$$

and where A and B are constants containing d and the well depth. Using the two conditions that characterize the energy minimum, $(r_0, -\epsilon)$, Eq. (7) can be expressed as

$$\epsilon = \frac{\epsilon \{ [3r_0^* P_0^{*(4)} + P_0^{*(3)}] P^{*(9)} - [9r_0^* P_0^{*(10)} + P_0^{*(9)}] P^{*(3)} \}}{[9P_0^{*(8)} P_0^{*(10)} - 3P_0^{*(4)} P_0^{*(9)}] r_0^*}, \quad (9)$$

in which $r^* \equiv r/d$ and $P_0^{*(N)} \equiv P_0^N d^N$. Let us examine a few of the characteristics of this potential.

First, it can be shown that in the limit $r_0^* \rightarrow \infty$ (or

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TABLE II. Potential parameters for nonpolar, nonspherical molecules (LJ values indicated by $r_0^* = \infty$).

Compound	r_0^*	$\epsilon/k(^{\circ}\text{K})$	$r_0(\text{\AA})$	$d(\text{\AA})$	σ^2	Reference
Benzene (280 to 438 $^{\circ}\text{K}$)	1.60	464	8.98	5.61	5.1×10^{-6}	a
	∞	183	11.6	0.00	7.2×10^{-4}	
Carbon dioxide (273 to 873 $^{\circ}\text{K}$)	1.40	607	3.62	2.59	4.4×10^{-4}	b
	∞	202	4.57	0.00	2.9×10^{-3}	
Cyanogen (308 to 423 $^{\circ}\text{K}$)	1.50	489	5.89	3.92	1.8×10^{-5}	c
	∞	174	7.74	0.00	3.0×10^{-5}	
Propadiene (293 to 353 $^{\circ}\text{K}$)	∞	195	7.20	0.00	6.0×10^{-6}	d
			(LJ potential gives better fit)			
Fluorine (80 to 250 $^{\circ}\text{K}$)	2.00	192	3.63	1.81	4.4×10^{-4}	e
	∞	97.4	4.63	0.00	1.3×10^{-3}	

^a R. J. L. Andon, J. D. Cox, E. F. G. Herrington, and J. F. Martin, *et al.*, *Trans. Faraday Soc.* **53**, 1074 (1957); J. D. Cox and R. J. L. Andon, *Trans. Faraday Soc.* **54**, 1622 (1958); A. E. Korveze, *Rec. trav. chim.* **72**, 483 (1953).

^b K. E. McCormack and W. G. Schneider, *J. Chem. Phys.* **18**, 1269 (1950).

^c Reference i, Table I.

^d Reference i, Table I.

^e D. White, J. Hu, and H. L. Johnston, *J. Chem. Phys.* **21**, 1149 (1953).

equivalently, $d \rightarrow 0$) the potential reduces smoothly to the Lennard-Jones potential. This can be seen by inserting the result

$$\lim_{r_0^* \rightarrow \infty} P_0^{*(N)} = N(N+1)r_0^{*-(N+2)} \quad (10)$$

into Eq. (9), obtaining

$$\phi = \frac{\epsilon[(60r_0^{*-5} + 12r_0^{*-5})90r_0^{*-11} - (990r_0^{*-11} + 90r_0^{*-11})12r_0^{*-5}]}{[9(12r_0^{*-5})(110r_0^{*-12}) - 3(20r_0^{*-8})(90r_0^{*-11})]r^*}, \quad (11)$$

which reduces to the Lennard-Jones potential.

Second, the rapidity with which the 12-6 result is approached as r_0^* increases can be seen from Fig. 2, where σ/r_0 is plotted as a function of r_0^* , (σ is the finite value of r for which $\phi=0$). The Lennard-Jones potential has the constant value $2^{-1/6}(0.89090)$.

Finally, a graphical comparison of the two potentials is made in Fig. 3, where the Lennard-Jones result is plotted along with the spherical shell potential ($r_0^*=2$) using a common well depth. The effect of shell integration is to narrow the well, an effect more pronounced as r_0^* approaches one.

2. CALCULATIONS

The result obtained when Eq. (9) is substituted into the standard expression for the second virial coefficient is not integrable analytically. When divided by

$$2\pi N_0 r_0^{*3}/3,$$

the second virial coefficient per mole becomes

$$B^*(r_0^*, T^*) = \frac{3}{r_0^{*3}} \int_0^{\infty} r^{*2} [1 - \exp(-\phi/\epsilon T^*)] dr^*, \quad (12)$$

where $T^* = kT/\epsilon$. This integral was evaluated by a

TABLE III. Potential parameters for polar molecules (LJ values indicated by $r_0^* = \infty$).

Compound	r_0^*	$\epsilon/k(^{\circ}\text{K})$	$r_0(\text{\AA})$	$d(\text{\AA})$	σ^2	Reference
Acetone (300 to 403 $^{\circ}\text{K}$)	1.20	817	8.90	7.41	3.3×10^{-4}	a
	∞	150	14.9	0.00	5.5×10^{-4}	
Methyl chloride (239 to 450 $^{\circ}\text{K}$)	1.50	566	5.47	3.65	3.7×10^{-5}	b
	∞	180	8.03	0.00	4.5×10^{-4}	
Methyl fluoride (273 to 423 $^{\circ}\text{K}$)	1.50	573	4.23	2.82	8.9×10^{-6}	c
	∞	183	6.13	0.00	1.2×10^{-4}	
Phenyl fluoride (318 to 623 $^{\circ}\text{K}$)	1.50	954	5.59	3.72	8.6×10^{-6}	d
	∞	250	9.72	0.00	4.2×10^{-4}	
Pyridine (347 to 438 $^{\circ}\text{K}$)	∞	184	12.6	0.00	9.4×10^{-5}	e
			(LJ potential gives better fit)			

^a J. S. Rowlinson, *Trans. Faraday Soc.* **45**, 974 (1949); J. D. Lambert, G. A. H. Roberts, J. S. Rowlinson, and V. J. Wilkinson, *Proc. Roy. Soc. (London)* **A196**, 113 (1949); R. E. Pennington and K. A. Kobe, *J. Am. Chem. Soc.* **79**, 300 (1957).

^b J. O. Hirschfelder, F. T. McClure, and I. F. Weeks, *J. Chem. Phys.* **10**, 201 (1942).

^c R. J. Lunbeck and C. A. ten Seldam, *Physica* **17**, 788 (1951).

^d D. R. Douslin, R. T. Moore, J. P. Dawson, and G. Waddington, *J. Am. Chem. Soc.* **80**, 2031 (1958).

^e Reference a, Table II; J. P. McCullough, D. R. Douslin, J. F. Messerly, I. A. Hossenlopp, T. C. Kincheloe, and G. Waddington, *J. Am. Chem. Soc.* **79**, 4289 (1957).

TABLE IV. Comparison of ϵ/k with critical temperatures.

Compound	r_0^*	$\epsilon/k(^{\circ}\text{K})$	$T_c(^{\circ}\text{K})$	ϵ/kT_c	Reference
Silicon tetrafluoride	1.30	621	259	1.6	a
Neopentane	1.50	811	434	1.9	b
Perfluorocyclobutane	1.50	599	388	1.5	c
Carbon tetrafluoride	1.70	322	228	1.4	d
Cyclopropane	1.70	635	398	1.6	e
Krypton	1.70	366	209	1.7	f
Sulfur hexafluoride	1.70	434	319	1.3	g
Tetramethylsilane	1.70	534	458	1.3	h
Sulfur hexafluoride	2.00	335	319	1.2	i
Methane	2.50	215	191	1.1	j
Xenon	3.00	292	290	1.0	k

^a S. D. Hamann and J. A. Lambert, *Australian J. Chem.* **7**, 1 (1954).

^b T. Ishikawa, *Bull. Chem. Soc. Japan* **28**, 515 (1955).

^c D. R. Douslin, R. T. Moore and G. Waddington, *J. Phys. Chem.* **63**, 1959 (1959).

^d See reference a, this table.

^e H. S. Booth and W. C. Morris, *J. Phys. Chem.* **62**, 875 (1958).

^f E. Mathias, C. A. Crommelin, and J. J. Meihuizen, *Physica* **4**, 1200 (1937).

^g See reference a, this table.

^h J. H. Perry, Editor, *Chemical Engineers' Handbook* (McGraw-Hill Book Company, Inc., New York, 1950), 3rd ed., p. 166.

ⁱ See reference a, this table.

^j K. S. Pitzer, D. Z. Lippmann, R. F. Curl, Jr., C. M. Huggins, and D. E. Petersen, *J. Am. Chem. Soc.* **77**, 3433 (1955).

^k See reference b, this table.

modification of the trapezoidal rule¹² to an estimated accuracy of 0.0001 in B^* . The values of r_0^* range from 1.2 to 4.0, and those for T^* from 0.2 to 400. In the Appendix the values of B^* are tabulated corresponding to the ranges cited above, and where, for comparison, the values for the Lennard-Jones potential are included (note that the 6-12 results included here are smaller by a factor of $\sqrt{2}$ than those compiled by Hirschfelder *et al.*,¹³ due to reduction by $2\pi N_0 r_0^3/3$ rather than $2\pi N_0 \sigma^3/3$).

The potential parameters were determined by a modification of the Lennard-Jones method,¹⁴ in which ΔT , ΔB , and r_0^* (from among those tabulated), were chosen to minimize

$$\sigma^2(r_0^*, \Delta T, \Delta B) = \frac{1}{M-1} \sum_{j=1}^M [\log B_j(T_j) - \Delta B - \log B_j^*(r_0^*, \log T_j - \Delta T)]^2, \quad (13)$$

consistent with M data points. This amounts to minimizing the sum of the squares of the vertical deviations on a $\log |B|$ vs $\log T$ plot. The quantities ΔT and ΔB are related to the potential parameters by the expressions

$$\Delta T = \log(\epsilon/k), \quad \Delta B = \log\left(\frac{2}{3}\pi N_0 r_0^3\right). \quad (14)$$

In many cases a subjective choice of the parameters by visual comparison results in two or more sets of constants, and to avoid this problem we chose to select

¹² W. E. Milne, *Numerical Calculus* (Princeton University Press, Princeton, New Jersey, 1949), p. 119.

¹³ Reference 1, p. 1114.

¹⁴ J. E. Lennard-Jones, *Proc. Roy. Soc. (London)* **A106**, 463 (1924).

those parameters for which the computer determined σ^2 to be a minimum; this results in an unambiguous assignment of the potential parameters.

In Table I the results for spherical nonpolar molecules are presented; in Table II, nonspherical, nonpolar molecules and in Table III, polar molecules. It should be noted that in only two cases—pyridine and propadiene—does the Lennard-Jones potential seem better, and for both of these the temperature range was small, less than 100°. The majority of the results indicate that the spherical shell potential is a general improvement over the Lennard-Jones potential, when the second virial coefficient is the discriminant.

3. COMPARISONS WITH EXPERIMENT

The improved agreement noted above could be misleading, since the three parameter spherical shell potential is certainly more flexible than the Lennard-Jones. The view that the spherical shell model represents an improvement can be better supported by comparisons with other types of data. It would be nice if comparisons with transport properties were possible, but the effort required to evaluate the collision integrals does not seem justified at present. It might be expected that transport properties for the spherical shell model would compare reasonably with experiment, since such

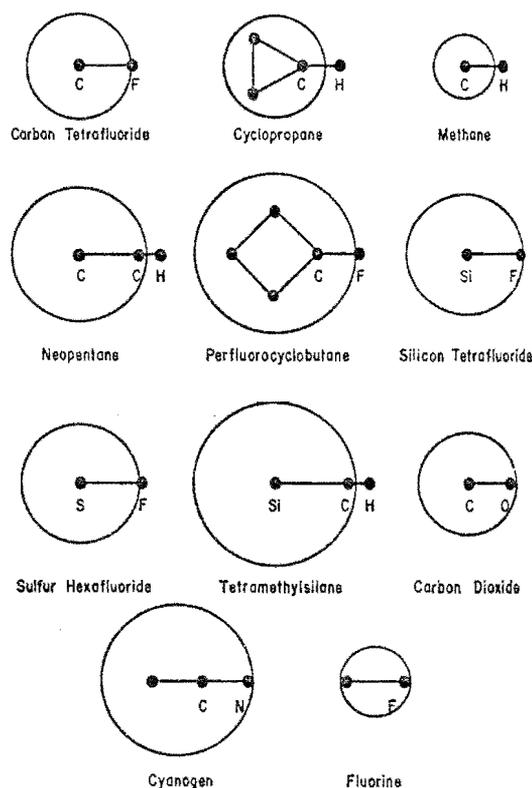


FIG. 4. Comparison of experimental intramolecular distances with the spherical shell diameter d as determined from second virial coefficient data. [Small circles \odot are drawn to represent distance from the molecular centers. Large circles of diameter d (to the same scale) are included for each compound.]

Carbon
Cyclop
Krypto
Methar
Neopen
Periluo
Silicon
Sulfur
Tetram
Xenon

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^b See
^c C. D
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^e See
^f D. B
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TABLE V. Values of r_0 from density and virial coefficient data.

Compound	Temperature	Density (g/cc)	r_0 , density	(All r_0 given in Å)		Reference
				$r_{0\text{ LJ}}$	$r_{0\text{ ss}}$	
Carbon tetrafluoride	-184°C (mp)	1.96	4.72	5.29	4.55	a
Cyclopropane	-79°C (L)	0.720	5.16	6.84	4.41	b
Krypton	-153°C (bp)	2.155	4.50	4.00	3.41	c
Methane	-164°C (L)	0.415	4.49	4.43	3.97	d
Neopentane	0°C (L)	0.613	6.51	8.49	5.26	e
Perfluorocyclobutane	30°C (L)	1.4506	6.87	7.92	6.22	f
Silicon tetrafluoride	-87°C (L)	1.629	5.31	6.31	4.12	g
Sulfur hexafluoride	-39°C (L)	1.79	5.76	6.35	5.18	h
Tetramethylsilane	20°C (L)	0.645	6.85	9.80	7.16	i
Xenon	-109°C (bp)	3.06	4.65	4.61	4.30	j

mp, melting point; bp, boiling point; L, liquid

* N. A. Lange, Editor, *Handbook of Chemistry* (McGraw-Hill Book Company, Inc., New York, 1961), 10th ed., p. 452.

^b See reference a, this table, p. 470.

^c C. D. Hodgman, Editor, *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1959), 41st ed., p. 590.

^d See reference c, this table, p. 1090.

^e See reference c, this table, p. 1176.

^f D. R. Douslin, R. T. Moore, and G. Waddington, *J. Phys. Chem.* **63**, 1959 (1959).

^g J. H. Simons, Editor, *Fluorine Chemistry* (Academic Press Inc., New York, 1950), Vol. I, p. 77-118.

^h See reference a, this table, p. 316.

ⁱ See reference c, this table, p. 1220.

^j See reference a, this table, p. 328.

comparisons are known for the 7-28 potential¹⁵ which, like the spherical shell potential, has a deeper and narrower well than the corresponding 6-12 potential. Subsequently, we will restrict ourselves to the following kinds of data: (1) the critical temperatures of the compounds in question, (2) values of r_0 obtained from the density of the liquid, assuming a closest-packed arrangement, (3) the known interatomic distances in the molecules.

For molecules having the same value of r_0^* , a corresponding states argument can be constructed from which one infers that $T_c^*(kT_c/\epsilon)$ should be a constant. The relevant information for the spherically symmetric molecules is contained in Table IV. A general decrease in ϵ/kT_c with increasing r_0^* is evident, and serves to emphasize the fact that the attractive part of the well is less important as the well becomes narrower. Assuming the experimental data to be correct and the potential reasonable, the behavior noted in the entries for ϵ/kT_c in Table IV may reflect the fact that the nearest neighbor separation is much smaller at the critical point than at the low densities used to determine $B(T)$. In the critical region the potential is surely dependent upon angle as well as distance.

One would expect the intermolecular separations in a liquid at low temperatures to be on the order of r_0 . It is true that vibrations tend to increase the separation, but the effect of neighbors beyond the first coordination shell is to diminish the separation; since both

effects are small,¹⁶ we will neglect them. We have used the density data entered in Table V to compute r_0 based on the assumption of closest-packing. The values of r_0 were determined from the easily derived equation, $r_0 = 1.329(M/D)^{1/3}$, where M is the molecular weight, D the density in g/cc, and r_0 is in Angstroms. Also included in Table V are the values of r_0 from the spherical shells potential and from the Lennard-Jones potential. Assuming that the nearest-neighbor separation is r_0 , it is clear that the value of r_0 computed for the closest-packed arrangement is an upper bound on r_0 , because for a less efficient packing the molecules are necessarily smaller. For several of the compounds listed in Table V, the Lennard-Jones value of r_0 greatly exceeds the closest-packed value, while the values from the spherical shells potential are generally smaller and thus in better agreement with our expectations.

Finally, interatomic distances are known quite accurately from x-ray and electron diffraction, and we may compare these data¹⁷ with the values of d determined from virial coefficient data for the spherical shell potential. In Fig. 4 we have drawn schematically the

¹⁶ Reference 1, p. 1036.

¹⁷ D. R. Douslin, R. T. Moore and G. Waddington, *J. Phys. Chem.* **63**, 1959 (1959), C₂F₆; H. Braune and S. Knoke, *Z. physik. Chem.* **21B**, 297 (1933), SF₆; the remainder from, L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948), 2nd ed.; A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, New York, 1950), 2nd ed.; Y. K. Syrkin and M. E. Dyatkina, *Structure of Molecules and the Chemical Bond* (Butterworths Scientific Publications, London, 1950).

¹⁵ J. C. McCoubrey and N. M. Singh, *Trans. Faraday Soc.* **55**, 826 (1959).

$\frac{r_0^*}{T^*}$

	1.20	1.30	1.40	1.50	1.60	1.70	1.80
0.20	-19.01515	-26.34844	-32.37243	-37.37132	-41.56609	-45.12462	-48.17413
0.21	-15.40027	-21.42153	-26.37016	-30.47788	-33.92546	-36.85057	
0.22	-12.70483	-17.74666	-21.89228	-25.33440	-28.22391	-30.67581	
0.23	-10.64719	-14.94042	-18.47212	-21.40532	-23.86801	-25.95802	
0.24	-9.04374	-12.75291	-15.80550	-18.34140	-20.47093	-22.27840	
0.25	-7.77132	-11.01647	-13.68827	-15.90841	-17.77306	-19.35590	-20.71304
0.26	-6.74523	-9.61574	-11.98001	-13.94507	-15.59575	-16.99712	
0.27	-5.90585	-8.46950	-10.58185	-12.33792	-13.81323	-15.06583	
0.28	-5.21035	-7.51944	-9.42274	-11.00532	-12.33510	-13.46424	
0.29	-4.62740	-6.72289	-8.45069	-9.88764	-11.09521	-12.12068	
0.30	-4.13370	-6.04807	-7.62703	-8.94046	-10.04433	-10.98184	-11.78590
0.32	-3.34774	-4.97327	-6.31479	-7.43108	-8.36950	-9.16661	
0.34	-2.75481	-4.16196	-5.32385	-6.29097	-7.10416	-7.79496	
0.35	-2.51107	-3.82829	-4.91620	-5.82187	-6.58342	-7.23044	-7.78547
0.36	-2.29509	-3.53254	-4.55481	-5.40592	-6.12169	-6.72982	
0.38	-1.93032	-3.03286	-3.94403	-4.70284	-5.34107	-5.88340	
0.40	-1.63516	-2.62830	-3.44936	-4.13326	-4.70859	-5.19748	-5.61699
0.42	-1.39224	-2.29517	-3.04190	-3.66400	-4.18738	-4.63220	
0.44	-1.18936	-2.01683	-2.70133	-3.27170	-3.75162	-4.15950	
0.45	-1.10010	-1.89432	-2.55139	-3.09895	-3.55968	-3.95129	-4.28738
0.46	-1.01776	-1.78128	-2.41303	-2.93953	-3.38255	-3.75913	
0.48	-0.87096	-1.57968	-2.16623	-2.65510	-3.06653	-3.41625	
0.50	-0.74413	-1.40543	-1.95285	-2.40917	-2.79320	-3.11965	-3.39981
0.52	-0.63358	-1.25350	-1.76673	-2.19459	-2.55471	-2.86085	
0.54	-0.53646	-1.11996	-1.60311	-2.00594	-2.34500	-2.63324	
0.55	-0.49221	-1.05910	-1.52854	-1.91993	-2.24939	-2.52948	-2.76987
0.56	-0.45052	-1.00175	-1.45825	-1.83887	-2.15927	-2.43165	
0.58	-0.37400	-0.89645	-1.32917	-1.68999	-1.99373	-2.25196	
0.60	-0.30545	-0.80210	-1.21349	-1.55655	-1.84534	-2.09087	-2.30162
0.65	-0.16192	-0.60444	-0.97105	-1.27680	-1.53421	-1.75307	-1.94092
0.70	-0.04842	-0.44800	-0.77911	-1.05526	-1.28774	-1.48542	-1.65510
0.75	+0.04344	-0.32132	-0.62358	-0.87568	-1.08793	-1.26841	-1.42333
0.80	0.11923	-0.21674	-0.49515	-0.72737	-0.92288	-1.08910	-1.23179
0.85	0.18276	-0.12903	-0.38739	-0.60289	-0.78431	-0.93858	-1.07097
0.90	0.23674	-0.05445	-0.29575	-0.49700	-0.66643	-0.81048	-0.93415
0.95	0.28316	+0.00970	-0.21690	-0.40588	-0.56497	-0.70023	-0.81633
1.00	0.32347	0.06543	-0.14836	-0.32666	-0.47675	-0.60436	-0.71386
1.05	0.35879	0.11429	-0.08827	-0.25719	-0.39938	-0.52026	-0.62401
1.10	0.38998	0.15745	-0.03518	-0.19579	-0.33099	-0.44592	-0.54456
1.15	0.41772	0.19585	+0.01208	-0.14115	-0.27012	-0.37975	-0.47385
1.20	0.44254	0.23022	0.05437	-0.09223	-0.21561	-0.32049	-0.41051
1.25	0.46488	0.26115	0.09245	-0.04818	-0.16653	-0.26713	-0.35345
1.30	0.48507	0.28913	0.12691	-0.00832	-0.12211	-0.21883	-0.30181
1.35	0.50342	0.31456	0.15822	+0.02791	-0.08173	-0.17492	-0.25487
1.40	0.52016	0.33776	0.18679	0.06098	-0.04488	-0.13484	-0.21203
1.45	0.53548	0.35901	0.21297	0.09128	-0.01110	-0.09810	-0.17275
1.50	0.54957	0.37855	0.23705	0.11914	+0.01996	-0.06432	-0.13664

TABLE VI (continued)

$T^* \times 10^3$	1.20	1.30	1.40	1.50	1.60	1.70	1.80
1.55	0.56255	0.39656	0.25924	0.14484	0.04860	-0.03317	-0.10331
1.60	0.57456	0.41322	0.27977	0.16861	0.07511	-0.00434	-0.07249
1.65	0.58569	0.42867	0.29882	0.19066	0.09970	+0.02241	-0.04387
1.70	0.59604	0.44304	0.31653	0.21117	0.12256	0.04729	-0.01727
1.75	0.60568	0.45642	0.33304	0.23028	0.14388	0.07048	+0.00753
1.80	0.61468	0.46893	0.34846	0.24815	0.16380	0.09216	0.03071
1.85	0.62311	0.48063	0.36289	0.26487	0.18246	0.11245	0.05241
1.90	0.63101	0.49161	0.37644	0.28056	0.19995	0.13149	0.07278
1.95	0.63843	0.50193	0.38916	0.29530	0.21639	0.14939	0.09194
2.00	0.64542	0.51163	0.40114	0.30918	0.23188	0.16624	0.10995
2.10	0.65821	0.52943	0.42310	0.33462	0.26027	0.19713	0.14299
2.20	0.66965	0.54534	0.44273	0.35738	0.28566	0.22478	0.17257
2.30	0.67993	0.55964	0.46039	0.37785	0.30851	0.24964	0.19918
2.40	0.68921	0.57255	0.47634	0.39635	0.32915	0.27211	0.22322
2.50	0.69762	0.58427	0.49082	0.41313	0.34788	0.29251	0.24506
2.60	0.70529	0.59495	0.50401	0.42843	0.36496	0.31110	0.26495
2.70	0.71229	0.60470	0.51607	0.44242	0.38058	0.32811	0.28315
2.80	0.71871	0.61366	0.52713	0.45525	0.39491	0.34372	0.29986
2.90	0.72462	0.62189	0.53732	0.46707	0.40811	0.35810	0.31525
3.00	0.73007	0.62950	0.54672	0.47798	0.42030	0.37138	0.32946
	0.73511	0.63653	0.55542	0.48808	0.43158	0.38366	0.34263
3.20	0.73978	0.64305	0.56349	0.49745	0.44205	0.39507	0.35484
3.30	0.74413	0.64912	0.57100	0.50617	0.45179	0.40569	0.36620
3.40	0.74817	0.65477	0.57799	0.51429	0.46087	0.41558	0.37679
3.50	0.75195	0.66005	0.58452	0.52188	0.46935	0.42482	0.38669
3.60	0.75548	0.66498	0.59064	0.52898	0.47729	0.43347	0.39595
3.70	0.75878	0.66961	0.59636	0.53564	0.48472	0.44158	0.40463
3.80	0.76188	0.67394	0.60174	0.54188	0.49171	0.44919	0.41280
3.90	0.76480	0.67802	0.60679	0.54776	0.49828	0.45636	0.42048
4.00	0.76754	0.68186	0.61156	0.55329	0.50447	0.46311	0.42771
5.00	0.78796	0.71050	0.64711	0.59466	0.55077	0.51362	0.48184
6.00	0.80040	0.72803	0.66893	0.62011	0.57929	0.54477	0.51527
7.00	0.80853	0.73954	0.68330	0.63690	0.59817	0.56540	0.53743
8.00	0.81408	0.74745	0.69322	0.64852	0.61123	0.57973	0.55284
9.00	0.81800	0.75306	0.70028	0.65683	0.62060	0.59001	0.56392
10.00	0.82081	0.75713	0.70544	0.66291	0.62748	0.59758	0.57208
20.00	0.82745		0.71915		0.64679		0.59572
30.00	0.82502		0.71647		0.64436		0.59365
40.00	0.82160		0.71171		0.63898		0.58796
50.00	0.81827		0.70687		0.63334		0.58186
60.00	0.81520		0.70235		0.62801		0.57605
70.00	0.81242		0.69821		0.62311		0.57068
80.00	0.80990		0.69443		0.61862		0.56575
90.00	0.80760		0.69098		0.61451		0.56123
100.00	0.80549		0.68781		0.61073		0.55707

$T^* r_0^*$

	1.90	2.00	2.50	3.00	3.50	4.00	∞
0.20	-50.81140	-53.11074	-61.18707	-65.93794	-68.96934	-71.01542	
0.25	-21.88694	-22.91079	-26.50849	-28.62530	-29.97601	-30.88758	
0.30	-12.48167	-13.08858	-15.22182	-16.47722	-17.27821	-17.81879	-19.71454
0.35	-8.26592	-8.68500	-10.15840	-11.02558	-11.57886	-11.95227	-13.26171
0.40	-5.98012	-6.29693	-7.41090	-8.06659	-8.48491	-8.76718	-9.75725
0.45	-4.57829	-4.83215	-5.72478	-6.25017	-6.58537	-6.81155	-7.60491
0.50	-3.64239	-3.85405	-4.59838	-5.03648	-5.31598	-5.50458	-6.16611
0.55	-2.97800	-3.15963	-3.79833	-4.17423	-4.41407	-4.57591	-5.14355
0.60	-2.48408	-2.64330	-3.20326	-3.53286	-3.74312	-3.88496	-4.38263
0.65	-2.10358	-2.24552	-2.74466	-3.03845	-3.22583	-3.35227	-3.79588
0.70	-1.80201	-1.93020	-2.38102	-2.64637	-2.81563	-2.92984	-3.33050
0.75	-1.55744	-1.67419	-2.08608	-2.32831	-2.48281	-2.58705	-2.95283
0.80	-1.35533	-1.46313	-1.84222	-2.06531	-2.20761	-2.30362	-2.64050
0.85	-1.18563	-1.28565	-1.63740	-1.84440	-1.97643	-2.06551	-2.37808
0.90	-1.04118	-1.13460	-1.46305	-1.65634	-1.77961	-1.86277	-2.15463
0.95	-0.91684	-1.00454	-1.31289	-1.49435	-1.61006	-1.68817	-1.96216
1.00	-0.80869	-0.89142	-1.18230	-1.35344	-1.46262	-1.53625	-1.79469
1.05	-0.71383	-0.79219	-1.06770	-1.22980	-1.33319	-1.40295	-1.64771
1.10	-0.62995	-0.70446	-0.96638	-1.12045	-1.21873	-1.28505	-1.51772
1.15	-0.55529	-0.62634	-0.87613	-1.02309	-1.11680	-1.18004	-1.40194
1.20	-0.48840	-0.55636	-0.79531	-0.93586	-1.02551	-1.08596	-1.29821
1.25	-0.42818	-0.49336	-0.72251	-0.85729	-0.94324	-1.00123	-1.20475
1.30	-0.37365	-0.43633	-0.65659	-0.78615	-0.86876	-0.92449	-1.12013
1.35	-0.32408	-0.38446	-0.59665	-0.72143	-0.80103	-0.85471	-1.04316
1.40	-0.27883	-0.33712	-0.54191	-0.66236	-0.73917	-0.79099	-0.97287
1.45	-0.23736	-0.29371	-0.49174	-0.60821	-0.68248	-0.73258	-0.90843
1.50	-0.19920	-0.25379	-0.44560	-0.55841	-0.63031	-0.67884	-0.84915
1.55	-0.16402	-0.21697	-0.40304	-0.51243	-0.58218	-0.62927	-0.79445
1.60	-0.13146	-0.18290	-0.36362	-0.46990	-0.53765	-0.58335	-0.74381
1.65	-0.10125	-0.15129	-0.32707	-0.43040	-0.49633	-0.54076	-0.69682
1.70	-0.07315	-0.12188	-0.29303	-0.39368	-0.45785	-0.50114	-0.65310
1.75	-0.04694	-0.09446	-0.26133	-0.35943	-0.42199	-0.46420	-0.61231
1.80	-0.02245	-0.06882	-0.23169	-0.32743	-0.38846	-0.42964	-0.57419
1.85	+0.00047	-0.04482	-0.20392	-0.29745	-0.35706	-0.39730	-0.53849
1.90	0.02198	-0.02231	-0.17787	-0.26930	-0.32758	-0.36693	-0.50498
1.95	0.04222	-0.00114	-0.15339	-0.24286	-0.29990	-0.33836	-0.47347
2.00	0.06126	+0.01880	-0.13031	-0.21792	-0.27381	-0.31149	-0.44380
2.10	0.09618	0.05535	-0.08800	-0.17224	-0.22594	-0.26218	-0.38936
2.20	0.12742	0.08805	-0.05014	-0.13134	-0.18311	-0.21805	-0.34062
2.30	0.15553	0.11748	-0.01608	-0.09454	-0.14455	-0.17830	-0.29676
2.40	0.18095	0.14410	+0.01473	-0.06127	-0.10971	-0.14235	-0.25709
2.50	0.20401	0.16824	0.04269	-0.03104	-0.07804	-0.10974	-0.22105

Table VI (continued)

$\frac{r_0^*}{T^*}$	1.90	2.00	2.50	3.00	3.50	4.00	∞
2.60	0.22504	0.19026	0.06821	-0.00347	-0.04917	-0.07998	-0.18818
2.70	0.24429	0.21040	0.09155	+0.02175	-0.02274	-0.05274	-0.15810
2.80	0.26195	0.22889	0.11298	0.04490	+0.00154	-0.02773	-0.13047
2.90	0.27821	0.24593	0.13272	0.06625	0.02390	-0.00469	-0.10501
3.00	0.29325	0.26167	0.15095	0.08595	0.04454	+0.01661	-0.08148
3.10	0.30716	0.27625	0.16783	0.10423	0.06367	0.03634	-0.05969
3.20	0.32006	0.28977	0.18353	0.12117	0.08145	0.05465	-0.03945
3.30	0.33207	0.30235	0.19812	0.13697	0.09797	0.07169	-0.02061
3.40	0.34328	0.31408	0.21174	0.15168	0.11341	0.08760	-0.00303
3.50	0.35375	0.32504	0.22445	0.16543	0.12783	0.10245	+0.01340
3.60	0.36355	0.33531	0.23637	0.17830	0.14133	0.11638	0.02879
3.70	0.37273	0.34494	0.24753	0.19038	0.15400	0.12944	0.04323
3.80	0.38136	0.35397	0.25802	0.20174	0.16590	0.14170	0.05680
3.90	0.38948	0.36248	0.26788	0.21242	0.17709	0.15327	0.06957
4.00	0.39713	0.37050	0.27719	0.22251	0.18764	0.16414	0.08161
4.10		0.37806	0.28598	0.23200	0.19760	0.17442	0.09298
4.20		0.38520	0.29428	0.24098	0.20702	0.18412	0.10372
4.30		0.39196	0.30214	0.24948	0.21593	0.19330	0.11389
4.40		0.39835	0.30958	0.25753	0.22438	0.20201	0.12352
4.50		0.40443	0.31663	0.26516	0.23240	0.21028	0.13267
4.60		0.41019	0.32332	0.27241	0.24000	0.21812	0.14135
4.70		0.41567	0.32968	0.27929	0.24722	0.22558	0.14960
4.80		0.42087	0.33574	0.28585	0.25410	0.23268	0.15746
4.90		0.42582	0.34150	0.29211	0.26065	0.23943	0.16494
5.00	0.45442	0.43054	0.34700	0.29806	0.26689	0.24587	0.17207
6.00	0.48982	0.46768	0.39025	0.34493	0.31609	0.29663	0.22833
7.00	0.51331	0.49233	0.41904	0.37619	0.34890	0.33050	0.26593
8.00	0.52966	0.50951	0.43917	0.39805	0.37189	0.35425	0.29234
9.00	0.54144	0.52189	0.45371	0.41390	0.38857	0.37149	0.31155
10.00	0.55012	0.53104	0.46452	0.42568	0.40097	0.38432	0.32589
20.00	0.57555	0.55807	0.49732	0.46201	0.43958	0.42447	0.37150
30.00	0.57367	0.55636	0.49637	0.46159	0.43953	0.42467	0.37259
40.00	0.56789	0.55051	0.49040	0.45560	0.43355	0.41870	0.36669
50.00	0.56163	0.54412	0.48365	0.44869	0.42655	0.41165	0.35947
60.00	0.55564	0.53800	0.47710	0.44194	0.41969	0.40472	0.35229
70.00	0.55010	0.53232	0.47100	0.43564	0.41327	0.39822	0.34553
80.00	0.54501	0.52710	0.46538	0.42982	0.40733	0.39221	0.33926
90.00	0.54035	0.52231	0.46021	0.42446	0.40186	0.38667	0.33348
100.00	0.53605	0.51790	0.45545	0.41952	0.39682	0.38156	0.32815
200.00		0.48716	0.42222	0.38505	0.36163	0.34590	0.29093
300.00		0.46871	0.40231	0.36444	0.34061	0.32466	0.26879
400.00		0.45573	0.38835	0.35002	0.32593	0.30992	0.25339

nonpolar molecules together with a circle of diameter d , preserving the distance of all atoms from the center, but not angle. We see from Fig. 4 that d has about the size one would expect intuitively if d represented the diameter of the sphere swept out by the centers of the peripheral groups during rotation.

We have seen that the spherical shell potential, as an extension of the Lennard-Jones potential, is in general an improvement over the latter for fitting second virial coefficient data. Its distinguishing feature, r_0^* , permits one to calculate distance parameters, d and r_0 , which are in reasonable accord with other existing data. The energy parameter is harder to validate because comparisons must at present be made with data strongly dependent upon nonspherical contributions to the potential. Even in those cases where calculated results and available experimental data are not in close agreement, the spherical shell potential is interesting in its own right, and may well become more useful in the future as more virial coefficient data of better precision become available.

4. ACKNOWLEDGMENTS

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APPENDIX: VALUES OF THE SECOND VIRIAL COEFFICIENT FOR THE SPHERICAL SHELLS MODEL

In this appendix we cite the Table VI values of

$$B^*(r_0^*, T^*)$$

calculated according to Eq. (12). We have also included the Lennard-Jones values given by Hirschfelder *et al.*,¹³ divided by $\sqrt{2}$ because we are using r_0 , rather than σ , as a reduction parameter. These Lennard-Jones values correspond to $r_0^* = \infty$. The pertinent dimensionless quantities are

$$B^* = B / (2\pi N r_0^3 / 3), \quad r_0^* = r_0 / d, \quad \text{and} \quad T^* = kT / \epsilon.$$

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Active Nitrogen at High Pressure*

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A pure nitrogen afterglow has been studied spectroscopically at pressures up to 1 atm and up to several seconds after the discharge. The first positive bands of nitrogen continue to show an unchanged preferential enhancement of bands with $v' = 11$ at high pressure, but their decay with time, measured photoelectrically, indicates that at high pressure $N(^4S)$ atoms must be removed by a more rapid process than recombination in triple collisions; it is suggested that this may be a two-body reaction with an oxide of nitrogen. Forbidden radiation from O, N, and N_2 predominates over the first positive bands at high pressure, and a high degree of immunity toward deactivating collisions is shown to be required for the metastable states $N(^2P)$, $O(^1S)$, and $N_2(A^3\Sigma_u^-)$. The absolute intensity and decay of the forbidden radiation indicates that $O(^1S)$ must be created in the afterglow while $N(^2P)$, and to some extent $N_2(A^3\Sigma_u^+)$, survive from the discharge. The observations favor a long radiative lifetime near 1 sec for $N_2(A^3\Sigma_u^+)$.

I. INTRODUCTION

THE majority of work concerned with the active nitrogen afterglow has been carried out at pressures of a few millimeters of mercury or lower¹; in the present paper we describe observations made on a pure nitrogen afterglow at considerably higher pressures extending up to 1 atm. As a background to the work to be described, we briefly review some of the properties

of the low-pressure nitrogen afterglow. Specifically we discuss the Lewis-Rayleigh (LR) afterglow which is easily excited at low pressure; we do not discuss the "auroral" afterglow investigated by Kaplan.²

The LR afterglow at low pressure is distinguished by its long life and characteristic bright yellow emission which, in the visible, consists of first positive bands ($B^3\Pi_g - A^3\Sigma_u^+$) of N_2 originating near $v' = 11$, with a smaller secondary maximum at $v' = 6$. Bands with $v' > 12$ are not observed. Recent work³ has re-

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¹ S. K. Mitra, *Active Nitrogen—A New Theory* (Association for the Cultivation of Science, Calcutta, 1945).

² J. Kaplan, *Phys. Rev.* **54**, 176 (1938).

³ See, e.g., K. D. Bayes and G. B. Kistiakowsky, *J. Chem. Phys.* **32**, 992 (1960).

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