

Determination of Energy Parameters in Lennard-Jones Potentials from Second Virial Coefficients

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(Received June 12, 1972)

The energy parameters in Lennard-Jones 6-12 potential between atoms (hydrogen, oxygen, nitrogen and carbon) were estimated from second virial coefficients of diatomic gases (H_2 , O_2 , N_2 , NO and CO) and methane (CH_4), assuming the additivity of atomic potentials and the combination rules for unlike pairs. The results show that there is a certain relation between the two parameters (van der Waals radius, r_w and the parameter of the attractive part, e) when the calculated virial coefficients are in agreement with the experimental data over a wide range of temperature. According to the relation one can select reasonable sets of parameters for atoms, which reproduce the experimental virial coefficients. In general, the best fit values of r_w for H, N and C atom were somewhat greater than those usually adopted. As for H-H interaction the parameters obtained from the virial data of H_2 differ from those from CH_4 due presumably to deviation of simple additivity of atomic interactions. The relation between r_w and e is available for justification or estimation of the energy parameters in atomic potentials, since any given atomic potential may have parameters which satisfy the relation or we can determine one of the parameters by the use of the relation if the other is found from the other measurements.

§ 1. Introduction

Theoretical calculations on stable conformations of molecules have been developed successfully from small organic substances^{1)~3)} to large polypeptides^{4),5)} by the use of either classical interatomic potentials⁶⁾ or quantum mechanical orbital theories.⁷⁾ Both approaches are based on the principle that a stable conformation of a molecule would have a minimum energy computed from all the intra- and inter-atomic interactions. It is expected that the final conformation must eventually be the same regardless of the method used. There are, of course, problems concerning approximations which have to be imposed on practical computations of the energy, e.g., additivity of interatomic potentials in the classical method. One of them in the classical approach may be how to determine the energy parameters in semiempirical potential functions, which have an essential role in calculating the energy.^{8)~12)}

Once an interatomic potential function is assumed to be either Lennard-Jones 6-12 or Buckingham potential function, the parameters may be estimated by several ways, e.g., crystal packing, beam scattering, etc.¹³⁾ Since a simpler form of the potential function is desirable for computation of the energy of a complicated large polymer molecule, the 6-12 potential which has only two para-

meters is commonly used. The estimation of the parameters in the potential has been done by a number of researchers^{14),15)} according to the theoretical basis of the equation, that is, the attractive dispersion force by the Slater-Kirkwood equation,¹⁶⁾ and the repulsive term from van der Waals radii of the atoms,¹⁷⁾ and then the parameters have been adjusted by the crystal packing¹⁸⁾ and other experimental data.

One of the simple experimental results available to test the validity of the potential parameters may be the second virial coefficient of a gas composed of atoms in question, since the virial coefficient can be calculated from the interaction between constituent atoms. Of course, the determination of the parameters from the second virial coefficients is not so critical, although, on the contrary, a correct potential must give the proper virial coefficient. Even if the determination from the virial coefficient might not give the precise energy parameters, the results would be useful for the estimation of reasonable range of the parameters. With such a hope, the determination of the parameters in 6-12 potentials from the second virial coefficients of diatomic molecules, H_2 , O_2 , N_2 , NO , CO and methane has been done, assuming the additivity of atomic interactions.

§ 2. Calculating procedure

1) Potentials and molecular geometry

When two molecules of the same kind of atoms interact with each other, the interaction energy $\phi(R)$ at a fixed position may be expressed by the use of Lennard-Jones 6-12 potential as follows:

$$\phi(R) = \sum_{i,j} (d/r_{ij}^{12} - e/r_{ij}^6) = \sum_{i,j} E \{ (2r_w/r_{ij})^{12} - 2(2r_w/r_{ij})^6 \}, \quad (1)$$

where R is the distance between centers of the molecules, r_{ij} is the distance between i -th atom of one molecule and j -th atom of the other molecule, and d and e (or E and r_w) are the energy parameters. At a given separation of the two molecules, r_{ij} is a function of rotation of the molecule at the position, so that r_{ij} can easily be calculated when a molecular geometry is fixed. The angles of rotation and the distances for diatomic molecules are shown in Fig. 1 and the geometry of the molecules is given in Table I. As for methane, Euler angles

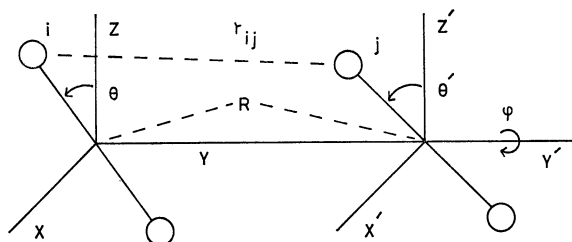


Fig. 1. The coordinate systems describing the mutual orientation of two diatomic molecules.

Table I. Bond lengths and bond angle.²³⁾

Molecule		
H ₂	H-H	0.7415 Å
O ₂	O-O	1.2074 Å
N ₂	N-N	1.0976 Å
CO	C-O	1.1282 Å
NO	N-O	1.150 Å
CH ₄	C-H	1.091 Å
	∠HCH	109.5°

were taken as variables. Furthermore, thermal effects on bond lengths and angles, permanent dipoles and quadrupoles were not taken into account.

2) Virial coefficient

The second virial coefficient $B(T)$ for a diatomic molecule is represented by the following equation:¹⁹⁾

$$B(T) = \frac{N}{4} \int_0^\infty \int_0^{2\pi} \int_0^\pi \int_0^\pi (1 - e^{-\phi(R, \theta, \theta', \varphi)/kT}) R^2 \sin \theta \sin \theta' d\theta d\theta' d\varphi dR, \quad (2)$$

where θ , θ' and φ are rotational angles shown in Fig. 1, N is Avogadro's number, k is the Boltzmann constant and T is the absolute temperature.

$B(T)$ for methane is expressed by

$$B(T) = \frac{2N}{\pi^2} \int_0^\infty \int_0^\pi \int_0^{\pi/2} \int_0^{\pi/2} \int_0^\pi \int_0^\pi (1 - e^{-\phi(R, \theta, \theta', \varphi, \varphi')/kT}) R^2 \\ \times \sin \theta \sin \theta' d\theta d\theta' d\varphi d\varphi' dR, \quad (3)$$

where θ , φ and ψ are Euler angles of one molecule and θ' and φ' are Euler angles of the other molecule.

Computation of $B(T)$ could be done by Eqs. (1) and (2) or (3), numerically, i.e., integrations were replaced by the summation at discrete positions with constant intervals of the variables, using Simpson's formula. The interval of R was chosen as 0.3 Å from R_{\max} to R_{\min} , where R_{\max} was the distance at which $\phi(R_{\max})$ had a value as small as -0.005 Kcal/mol and R_{\min} was chosen the separation distance for $\phi(R_{\min})$ greater than 15 Kcal/mol, and the intervals of angles were taken as 30° for diatomic gases, and 45° for methane, respectively. The errors in calculated virial coefficients arisen from the above approximations were within ca. 3% smaller than the experimental error of the virial data (ca. 10%).

3) Determination of energy parameters in 6-12 potentials

For the atomic interaction between different kinds of atoms, the combination rule²⁰⁾ was employed, i.e., van der Waals radius $r_{w,ij}$ and the attractive parameter e_{ij} for interaction between an i -th kind of atom and a j -th kind of atom may be written as follows:

$$r_{w,ij} = \frac{1}{2}(r_{w,ii} + r_{w,jj}), \quad (4)$$

$$e_{ij} = (e_{ii}e_{jj})^{1/2} \quad (5)$$

or

$$d_{ij} = e_{ij}(2r_{w,ij})^6/2. \quad (6)$$

The value of $B(T)$, then, may be computed as a function of r_w and e at a given temperature, and therefore we can find such a relation between r_w and e that the

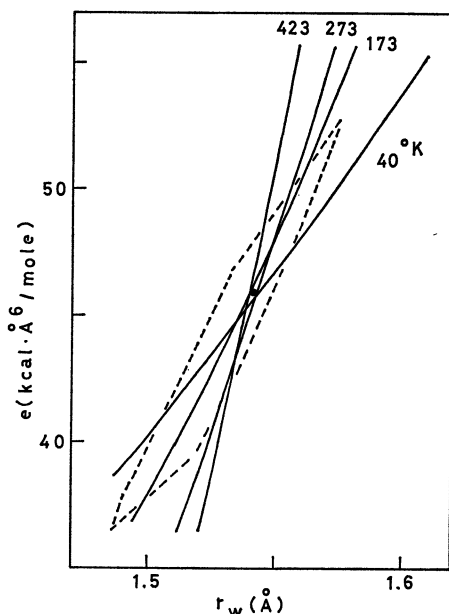


Fig. 2. The relations between r_w and e of H atom which give the experimental second virial coefficients of H_2 gas are shown at several temperatures. The closed area surrounded by a broken line represents the region where the deviation of the virial coefficients at the temperatures is within 10%. The closed circle is the best point for the experimental second virial coefficients for H_2 gas.

computed coefficient may coincide with the experimental datum at the temperature. Since the curve of r_w versus e was temperature dependent, the values of r_w and e could be determined from the region where every curves met together, for example, as shown in Fig. 2. When 10% or 20% deviation of the calculated virial coefficients from the experimental ones was allowed due to possible experimental errors and the approximation employed, we could find an overlap region (Fig. 2), from which the low and high limit of r_w and e were given. The computed virial coefficient by using the values of r_w and e thus determined is in agreement with the experiments. For NO molecule the curve of r_w versus e did not meet at a region, so that appropriate values were selected to test how to fit the experimental curves. For H_2 gas, the virial coefficients after the correction of quantum effect²¹⁾ were used.

All the computations were carried out by Facom 230-60 in the computing center of Kyoto University.

§ 3. Results

The curves shown in Fig. 2 demonstrate the relations between r_w and e of H atom derived from the virial data of H_2 molecule as a function of temperature. Along each line, the second virial coefficient at the temperature can be reproduced. Since the increase in r_w has the same effect as the increase in e (that is, deepening the potential) to give the same value of the virial coefficient, we cannot determine r_w and e at a temperature. However, when data of temperature dependence were taken into account, we could find a limited region of r_w and e independent of temperature as shown in Fig. 2, where the virial coefficients are in agreement with the data within 10% accuracy (dashed line). The parameters r_w and e of the best fit for the experimental curve were 1.54 Å and 46 Kcal Å⁶/mol, respectively (closed circle shown in Fig. 2), and Fig. 3 demonstrates the agreement of the computed virial coefficients with the experiments by using these values. The value of 1.54 Å for r_w seems to be somewhat greater than that usually adopted, but the potential curve for H_2 coincides with the experimental one by Michels et al.²¹⁾ (Fig. 4.) When a smaller value of r_w is taken, we must reduce the value of e in order to give the experimental $B(T)$ and the agreement becomes worse. The low and high limits of r_w and e for H atom are listed in Table II.

The range of r_w and e for O atom from the virial data of O_2 gas (Fig. 5) gives the best values of $r_w=1.66$ Å and $e=285$ Kcal Å⁶/mol, the values which

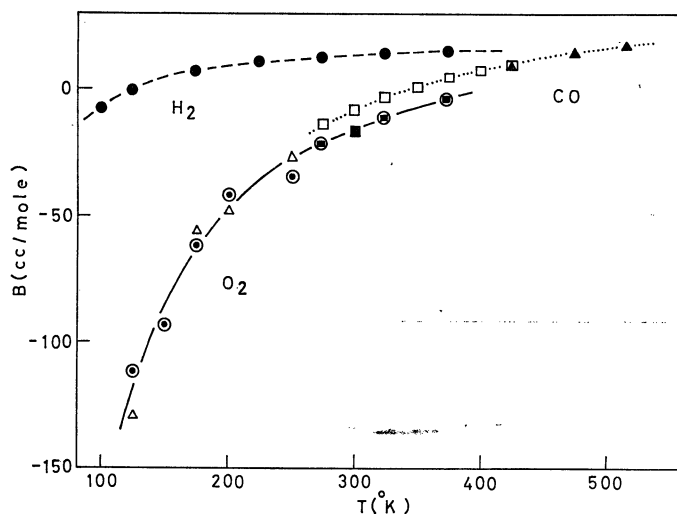


Fig. 3. Second virial coefficients for H_2 , O_2 and CO . Calculated curves for H_2 ($r_w=1.54$ Å and $e=46$ Kcal Å⁶/mol)---, for O_2 ($r_w=1.66$ Å and $e=285$ Kcal Å⁶/mol)—— and for CO ($r_w=2.10$ Å and $e=825$ Kcal Å⁶/mol for C atom, and $r_w=1.66$ Å and $e=285$ Kcal Å⁶/mol for O atom)..... Experimental data: H_2 , Ref. 21) (●); O_2 , Ref. 24) (△), Ref. 25) (○), Ref. 26) (○), Ref. 27) (■); CO , Ref. 28) (□), Ref. 29) (▲).

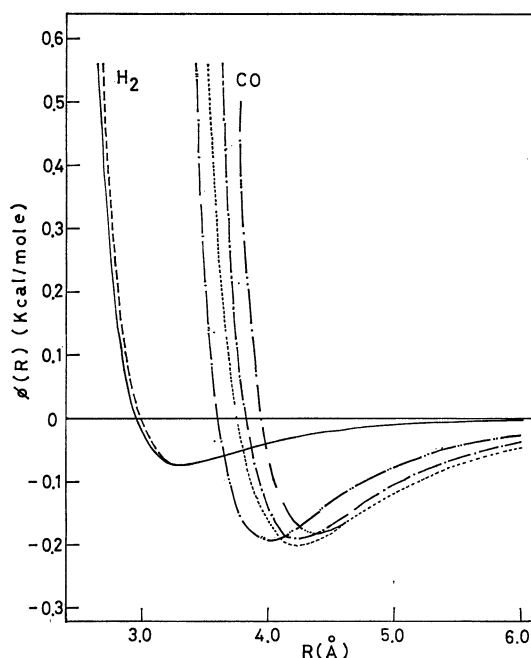


Fig. 4. Potential energy between two molecules as a function of the distance. H_2 ; Michels et al.²¹— and this study ($r_w=1.54$ Å and $e=46$ Kcal Å⁶/mol for H atom)——. CO; Hirschfelder et al.¹⁹..... and this study ($r_w=2.0$ Å and $e=580$ Kcal Å⁶/mol for C atom, $r_w=1.66$ Å and $e=285$ Kcal Å⁶/mol for O atom)—.—, ($r_w=1.82$ Å and $e=305$ Kcal Å⁶/mol for C atom, $r_w=1.66$ Å and $e=285$ Kcal Å⁶/mol for O atom)—.—, ($r_w=2.10$ Å and $e=825$ Kcal Å⁶/mol for C atom and $r_w=1.66$ Å and $e=285$ Kcal Å⁶/mol for O atom)—.—.

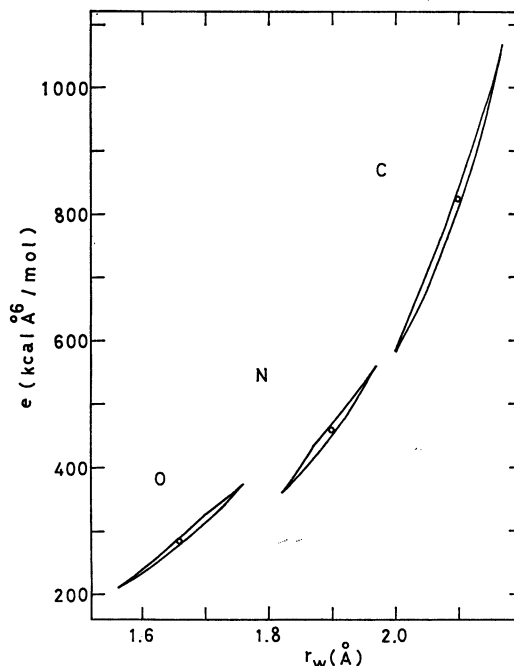


Fig. 5. Limited regions of r_w and e , obtained from the virial data, of O atom, N atom and C atom are shown. When the values of r_w and e within the regions are employed, the corresponding virial coefficients are reproduced with the accuracy of 10% (O_2 , N_2 and CO). The region for C atom was determined by the use of the midpoint of O-atom region. The midpoints (open circles) are the best-fit values.

provide the computed virial coefficients in a good coincidence with the experiments as demonstrated in Fig. 3. These parameters are close to the values commonly employed. The curves of r_w versus e were relatively insensitive of temperature, so that the range within 10% accuracy shown in Fig. 5 formed a narrow valley. The high limit of the range of r_w and e was found to be 1.76 Å and 375 Kcal Å⁶/mol, respectively (Table II).

By the use of the best fit parameters for O atom, the range of r_w and e for C atom was determined from $B(T)$ curves of CO molecule at several temperatures (Fig. 5). The best values may be $r_w=2.10$ Å and $e=825$ Kcal Å⁶/mol, which are the values higher than those usually employed.⁹ When the values at the low limit of 10% accuracy, $r_w=2.00$ Å and $e=580$ Kcal Å⁶/mol, are taken, the theoretical curve deviates slightly below 300°K and above 500°K. However,

Table II. Range of r_w and e determined from virial coefficients (10% accuracy).

atom	gas	low limit		midpoint		high limit	
		r_w (A)	e (Kcal A ⁶ /mol)	r_w (A)	e (Kcal A ⁶ /mol)	r_w (A)	e (Kcal A ⁶ /mol)
H	H ₂	1.48	36	1.54	46	1.58	53
	a)	1.17	19	1.27	24	1.37	33
	CH ₄ b)	1.20	19	1.30	27	1.38	35
	c)	1.25	23	1.32	30	1.38	37
O	O ₂	1.56	210	1.66	285	1.76	375
C	CO d)	2.00	580	2.10	825	2.17	1070
	e)	1.82	305	2.00	580	2.10	825
N	N ₂	1.82	360	1.90	455	1.97	560
		(1.75)	(290) ^{f)}			(2.02)	(645) ^{f)}

a) $r_w=2.10$ A and $e=825$ Kcal A⁶/mol for C atom.

b) $r_w=2.00$ A and $e=580$ Kcal A⁶/mol for C atom.

c) $r_w=1.82$ A and $e=305$ Kcal A⁶/mol for C atom.

d) $r_w=1.66$ A and $e=285$ Kcal A⁶/mol for O atom.

e) $r_w=1.76$ A and $e=375$ Kcal A⁶/mol for O atom.

f) limits of 20% accuracy.

these values are the best ones when the high limit of the parameters for O atom, $r_w=1.76$ A and $e=375$ Kcal A⁶/mol are employed. The high and low limits of r_w and e in this case are 2.10 A and 825 Kcal A⁶/mol, and 1.82 A and 305 Kcal A⁶/mol, respectively (Table II). The potential curves of CO for the three sets of the parameters described above are demonstrated in Fig. 4. As far as the potential curves concerned, the parameters for C atom seem to be somewhat between 1.82 A and 2.00 A for r_w and 305 Kcal A⁶/mol and 580 Kcal A⁶/mol for e .

The potential for N atom can be derived in two ways, one from $B(T)$ of N₂ gas and the other from $B(T)$ of NO by using the parameters of O atom described previously. However, experimental data indicate that it is impossible to choose reasonable energy parameters for N and O atoms so as to make coincidence of theoretical curves with the three experimental data of N₂, O₂ and NO simultaneously, since the experimental $B(T)$ curves of N₂ and O₂ are larger than that of NO as clearly seen in Table III. Therefore, we have tried in the above two ways to estimate the approximate parameters for N atom.

From the virial data of N₂ gas, the curves of r_w versus e met at a point where the values $r_w=1.90$ A and $e=455$ Kcal A⁶/mol gave the virial coefficients in excellent agreement with the experimental data (Figs. 6 and 8). The range within 10% accuracy of r_w and e was obtained from the curves in Fig. 6 (Fig. 5). The $B(T)$ curve of N₂ gas computed by the use of the parameters of low limit,

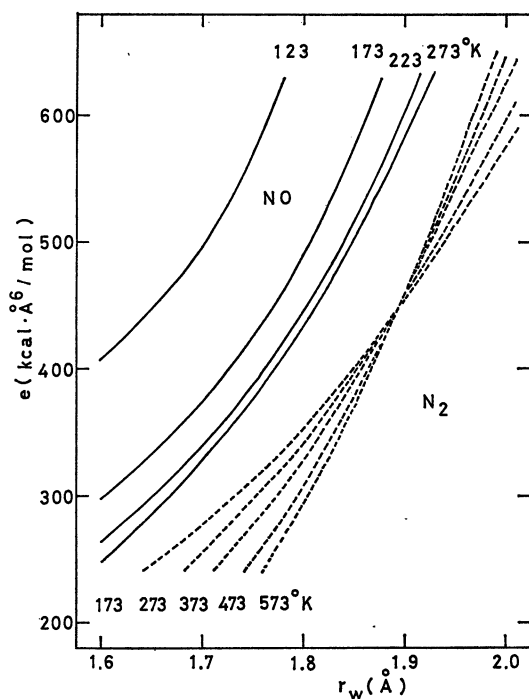


Fig. 6. The relations between r_w and e of N atom are shown as a function of temperature. The curves of N_2 gas meet at a point, but the curves of NO gas are almost parallel. The values of r_w and e along the curves can be reproduced by the second virial coefficients at the temperature. The best-fit values of O atom obtained from O_2 gas were used for evaluation of N atom in NO.

perimental data by the use of these parameters (Fig. 7).

The difficulty described above might be improved by further refinement of taking the dipole and quadrupole effects into account, but the corrections by the effects were not adequate to give a satisfactory agreement with the theoretical values. Presumably the additivity assumed would not sufficiently be accurate (see § 4).

Another simple molecule, CH_4 , is available for determination of energy parameters for H atom bonded to carbon. Since the parameters for C atom could not be uniquely determined from the virial data of CO gas, three sets of parameters were used to evaluate the parameters of H atom in CH_4 . We could determine the 10% accuracy region for the relation between r_w and e of H atom at a fixed set of the energy parameters of C atom and the results are listed in Table II. When the values of $r_w=1.30$ Å and $e=27$ Kcal Å⁶/mol for H atom and $r_w=2.00$ Å and $e=580$ Kcal Å⁶/mol for C atom were used, the theoretical

$r_w=1.75$ Å and $e=290$ Kcal Å⁶/mol, deviates below 200°K and above 400°K from the experimental data (Fig. 7). The $B(T)$ curve for NO gas by applying the parameters obtained for N and O atoms described here is higher than the experimental curve (Fig. 7).

In the other method, the curves of the relation between r_w and e computed from the virial data of NO gas by using the parameters of O atom ($r_w=1.66$ Å and $e=285$ Kcal Å⁶/mol) were parallel to each other as a function of the temperature and did not meet in a region as shown in Fig. 6, so that we could not choose proper values of the parameters for N atom. If, for example, $r_w=1.65$ Å and $e=310$ Kcal Å⁶/mol are taken as the parameters, the computed $B(T)$ curve is in agreement with the experimental curve in the temperature range above 150°K but deflects below the temperature. Of course, the computed curve for N_2 gas becomes much lower than the ex-

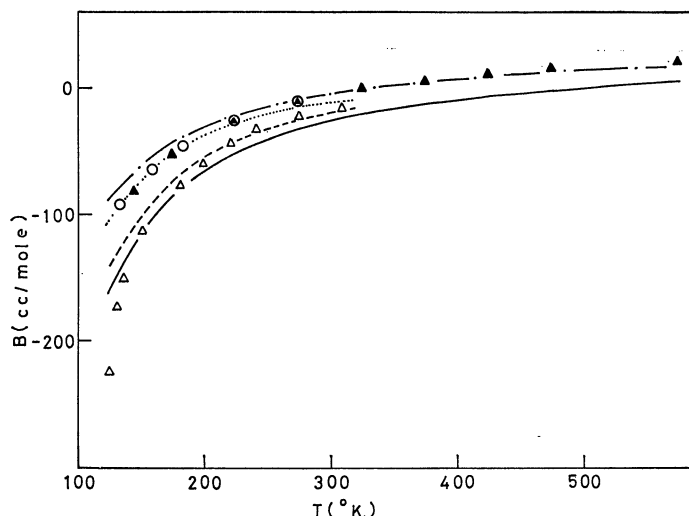


Fig. 7. Second virial coefficients for NO and N_2 . Calculated values for N_2 , —(A) and - - - (B); for NO, - - - (A) and (B). (A): $r_w=1.65$ Å and $e=310$ Kcal Å⁶/mol for N atom and $r_w=1.66$ Å and $e=285$ Kcal Å⁶/mol for O atom. (B): $r_w=1.75$ Å and $e=290$ Kcal Å⁶/mol for N atom and $r_w=1.66$ Å and $e=285$ Kcal Å⁶/mol for O atom. Experimental values for N_2 , Ref. 30) (○), Ref. 31) (▲), for NO, Ref. 32) (△).

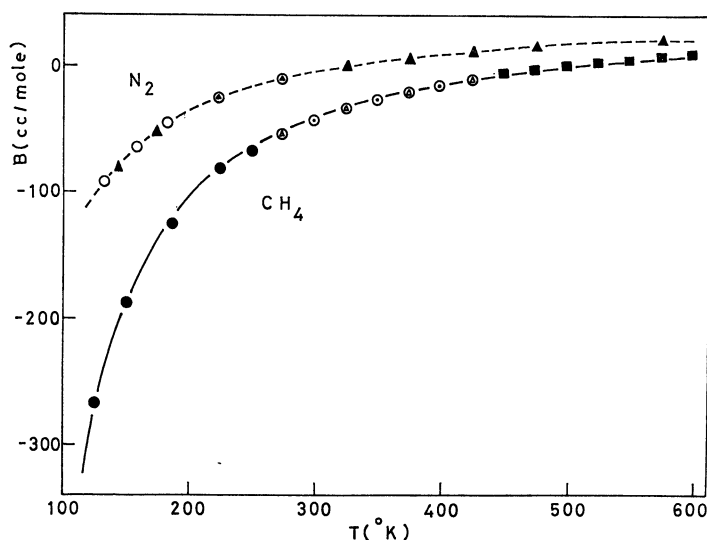


Fig. 8. Second virial coefficients for N_2 and CH_4 . Calculated curves for N_2 ($r_w=1.90$ Å and $e=455$ Kcal Å⁶/mol) - - - and for CH_4 ($r_w=2.00$ Å and $e=580$ Kcal Å⁶/mol for C atom and $r_w=1.30$ Å and $e=27$ Kcal Å⁶/mol for H atom) —. Experimental data: N_2 , Ref. 30) (○), Ref. 31) (▲); CH_4 , Ref. 33) (●), Ref. 34) (△), Ref. 35) (⊙), Ref. 36) (■).

curve of $B(T)$ was found to be in a satisfactory agreement with the experimental data as shown in Fig. 8. By using another set of parameters for C atom, $r_w=1.82$ Å and $e=305$ Kcal Å⁶/mol, the values of $r_w=1.32$ Å and $e=30$ Kcal Å⁶/mol for H

atom gave the best-fit curve of $B(T)$. According to the results, r_w of H atom is around 1.30 Å and e ca. 27 Kcal A⁶/mol. On the other hand the parameters of H atom determined from H₂ gas were too large to account for the virial data of CH₄.

§ 4. Discussion

The present results show that atomic potentials can be estimated from virial data using simple model of the molecule. It may be necessary to evaluate the order of corrections or effects ignored in the calculation such as thermal effect, dipole and quadrupole, which might give considerable alteration of the parameters.

First of all, the bond length assumed to be constant in the present calculation would be dependent on the temperature due to bond stretching. The mean square deviation of bond length $\langle(\Delta l)^2\rangle^{1/2}$ (Δl =difference between the equilibrium bond length l_0 and length l at a certain temperature) may be expressed by $1/2(RT/E_0)^{1/2}$, where E_0 is the stretching energy parameter in $E(l)=E_0(l_0-l)^2$. The deviation of bond length estimated from this relation by putting $E_0=300$ Kcal/A²mol¹) is only 0.02 Å at the room temperature and becomes less with decreasing temperature, so that the effect of bond stretching on the results is not necessary to be taken into account in the present calculation, since the analyses are not so accurate as to discuss the order of a few hundredths of angstrom.

Much larger factors necessary for the correction may be the effect of quadrupole and induced dipole of the atoms mentioned before. The corrections calculated according to Spurling and Mason²³⁾ are listed in Table III. At the room temperature contributions to the virial coefficient from the factors become larger in the sequence of O₂, N₂, CO and NO from -1.5 cc/mol to -5.9 cc/mol and the effect is greater with the decreasing temperature. These amounts of the correction do not have such an effect that brings significant changes in the range of r_w and e obtained without corrections. The contribution of permanent dipole of NO and CO was much more smaller. These corrections discussed here make r_w larger and e smaller.

The reason of discrepancy in obtaining inconsistent r_w and e for H atom from the virial data of H₂ and CH₄ is not clear. It might be inferred that the potential would be dependent on the nature of chemical bond which involves the atom questioned and especially the fact that H atom is the lightest one would have an effect. The present results also suggest the deviation of the simple additivity of atomic interactions especially for N and H. There is a possibility to account for the deviation by taking the bond order into consideration, since the localization of electrons in the atom would be altered by the nature of bond. Quantum mechanical treatment is required for such evaluation.

Notwithstanding the ambiguity discussed above the results obtained from the virial coefficients are useful for evaluation of the energy parameters, since any

Table III. Experimental second virial coefficients (in cc/mol) and the contribution of quadrupole-induced dipole (B_{q-d}) and quadrupole-quadrupole (B_{q-q}) interactions. ΔB represents the sum of both contributions.

$T(^{\circ}\text{K})$		123.2	173.2	198.2	223.2	273.2	298.2	323.2	373.2	423.2	473.2	513.2	573.2
N_2	$B_{\text{exp}}^{\text{a)}$	-106.0	-52.6		-26.7	-10.5		-0.3	6.2	11.7	15.6		20.9
	B_{q-d}	-13.1	-6.3		-3.8	-2.5		-1.9	-1.4	-1.1	-0.9		-0.7
	B_{q-q}	-2.5	-1.6		-1.2	-1.0		-0.9	-0.7	-0.7	-0.6		-0.5
	ΔB	-15.6	-7.9		-5.0	-3.5		-2.8	-2.1	-1.8	-1.5		-1.2
O_2	$B_{\text{exp}}^{\text{b)}$	-121.0	-65.0		-36.0	-22.2	-16.5	-11.8	-3.5				
	B_{q-d}	-4.7	-2.1		-1.2	-0.8	-0.7	-0.6	-0.4				
	B_{q-q}	-1.9	-0.9		-0.9	-0.7	-0.7	-0.6	-0.5				
	ΔB	-6.6	-3.0		-2.1	-1.5	-1.4	-1.2	-0.9				
NO	$B_{\text{exp}}^{\text{c)}$	-216.7	-81.3	-58.7	-42.1	-23.4							
	B_{q-d}	-24.3	-11.0	-8.2	-6.4	-4.2							
	B_{q-q}	-4.9	-3.0	-2.5	-2.2	-1.7							
	ΔB	-29.2	-14.0	-10.7	-8.6	-5.9							
CO	$B_{\text{exp}}^{\text{d)}$					-14.4	-8.4	-3.5	4.6	10.2	14.5	17.3	20.5
	B_{q-d}					-3.4	-2.9	-2.5	-1.9	-1.5	-1.3	-1.1	-0.9
	B_{q-q}					-1.6	-1.5	-1.4	-1.2	-1.1	-1.0	-0.9	-0.8
	ΔB					-5.0	-4.4	-3.9	-3.1	-2.6	-2.3	-2.0	-1.7

See Refs., a) 30)~31), b) 24)~27), c) 32) and d) 28)~29).

accurate potential function must give the correct virial coefficient. As expected from the nature of the virial coefficient, interatomic potential could not uniquely be determined at a given temperature, since an increase in r_w could be compensated by deepening the potential curve to give the same virial coefficient. Nevertheless, energy parameters of the atoms would be restricted within the narrow region where the calculated virial coefficient in a certain range of temperature fits the experimental data and at least the parameters must lie in the region. Once r_w or e is given by other techniques, e or r_w may be determined from the relation between r_w and e obtained in this study.

The estimation of r_w and e for diatomic molecules of different kind such as CO, NO and CH_4 may look like depending on the choice of r_w and e for the atom not questioned, i.e., O in CO, N in NO and C in CH_4 . However, because of the insensitivity of the virial coefficient in the region mentioned above, the final range of the atom was not changed significantly. As a consequence, the final region listed in Table II may be regarded as the proper region of the atoms.

In general, the best-fit values of r_w for all the atoms except O atom seem to be large compared with those used commonly by ca. 0.2 Å (see Table II), while the parameters in the low limit may be of the similar order although the deviation from the virial data is larger. We cannot decide which atomic energy parameters are better at the present stage.

The present work was supported partly by the research grant from the Institute of Fundamental Physics of Kyoto University.

References

- 1) M. Bixon and S. Lifson, *Tetrahedron* **23** (1967), 769.
- 2) S. Lifson and A. Warshel, *J. Chem. Phys.* **49** (1968), 5116.
- 3) J. B. Hendrickson, *J. Am. Chem. Soc.* **89** (1967), 7043, 7047.
- 4) T. Ooi, R. A. Scott, G. Vanderkooi and H. A. Scheraga, *J. Chem. Phys.* **46** (1967), 4410.
- 5) H. A. Scheraga, *Chem. Rev.* **71** (1971), 195; *Adv. Phys. Org. Chem.* **6** (1968), 103.
- 6) G. N. Ramachandran and V. Sasisekharan, *Adv. Protein Chem.* **23** (1968), 283.
- 7) B. Pullman, *Colloque International du CNRS*, ed. by R. Daudel and A. Pullman (Paris, 1971), p. 261.
- 8) L. S. Bartell, *J. Chem. Phys.* **32** (1960), 827.
- 9) D. E. Williams, *J. Chem. Phys.* **45** (1966), 3770.
- 10) J. B. Hendrickson, *J. Am. Chem. Soc.* **89** (1967), 7036.
- 11) J. L. DeCoen, G. Elefante, A. M. Liquori and A. Damiani, *Nature* **216** (1967), 910.
- 12) A. M. Liquori, E. Giglio and L. Mazzarella, *Nuovo Cim.* **55** (1968), B476.
- 13) J. O. Hirschfelder, "Intermolecular Forces", *Adv. Chem. Phys.* **12** (1967), 329.
- 14) D. A. Brant and P. J. Flory, *J. Am. Chem. Soc.* **87** (1965), 2791.
- 15) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.* **42** (1965), 2209.
- 16) J. C. Slater and J. G. Kirkwood, *Phys. Rev.* **37** (1931), 682.
- 17) A. Bondi, *J. Phys. Chem.* **68** (1964), 44.
- 18) A. I. Kitaigorodsky, *Acta Cryst.* **18** (1965), 585.
- 19) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 153.
- 20) E. A. Mason and T. H. Spurling, *Virial Equation of State* (Pergamon Press, 1969).
- 21) A. Michels, W. De Graaff and C. A. Ten Seldam, *Physica* **26** (1960), 393.
- 22) T. H. Spurling and E. A. Mason, *J. Chem. Phys.* **46** (1967), 322.
- 23) L. E. Sutton, ed., *Tables of Interatomic Distances and Configuration in Molecules and Ions* (Chem. Soc., London, 1958).
- 24) G. P. Nijhoff and W. H. Keesom, *Comm. Phys. Lab. Leiden* **179b** (1925).
- 25) D. White, J. -H. Hu and H. L. Johnston, *J. Chem. Phys.* **21** (1953), 1149.
- 26) L. Holborn and J. Otto, *Z. Phys.* **10** (1922), 367.
- 27) A. Michels, H. W. Jr. Schamp and W. De Graaff, *Physica* **20** (1954), 1209.
- 28) A. Michels, J. M. Lupton, T. Wassenaar and W. De Graaff, *Physica* **18** (1952), 121.
- 29) J. F. Connolly, *Phys. Fluids* **7** (1964), 1023.
- 30) A. E. Hoover, F. B. Canfield, R. Kobayashi and T. W. Jr. Leland, *J. Chem. Eng. Data* **9** (1964), 568.
- 31) L. Holborn and J. Otto, *Z. Phys.* **33** (1925), 1.
- 32) H. L. Johnston and H. R. Weimer, *J. Am. Chem. Soc.* **56** (1934), 625.
- 33) G. Thomaes and R. Van Steenwinkel, *Nature* **187** (1960), 229.
- 34) H. W. Jr. Schamp, E. A. Mason, A. C. B. Richardson and A. Altman, *Phys. Fluids* **1** (1958), 329.
- 35) A. Michels and G. W. Nederbragt, *Physica* **2** (1935), 1000.
- 36) D. R. Douslin, R. H. Harrison, R. T. Moore and J. P. McCullough, *J. Chem. Eng. Data* **9** (1964), 358.