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## van der Waals Volumes and Radii

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Intermolecular van der Waals radii of the nonmetallic elements have been assembled into a list of "recommended" values for volume calculations. These values have been arrived at by selecting from the most reliable X-ray diffraction data those which could be reconciled with crystal density at 0°K. (to give reasonable packing density), gas kinetic collision cross section, critical density, and liquid state properties. A qualitative understanding of the nature of van der Waals radii is provided by correlation with the de Broglie wave length of the outermost valence electron. Tentative values for the van der Waals radii of metallic elements—in metal organic compounds—are proposed. The paper concludes with a list of increments for the volume of molecules impenetrable to thermal collision, the so-called van der Waals volume, and of the corresponding increments in area per molecule.

### Table of Nomenclature

$A_w$	Surface area of molecules (based on model of Fig. 3) per mole (cm. <sup>2</sup> /mole)	$V_0$	Molal volume at 0°K.
$b$	Covalent bond radius, Å.	$V_c$	Molal volume at critical temperature and pressure
$C$	Normalization constant in eq. 1	$V_w$	van der Waals volume (calculated on the basis of Fig. 3)
$d_w$	Nonbonded internuclear distance between atoms of neighboring molecules	$Z$	Number of nearest neighbors of a molecule
$E^\circ$	Standard energy of vaporization, defined in ref. 2	$\delta(\ )$	Decrement of $V_w$ or $A_w$ (as indicated) due to intramolecular crowding or hydrogen bonding
$h$	Planck constant	$\lambda_B \equiv h\sqrt{m_e I_0}$	= de Broglie wave length of outermost valence electron
$I_0$	First ionization potential	$\rho_0^*$	$\equiv V_w/V_0$ = packing density at 0°K.
$l$	Bond distance, Å.	$\rho_c^*$	$\equiv V_w/V_c$ = packing density at critical point
$m_e$	Rest mass of an electron	$\sigma$	Distance between like atoms (molecules) at steepest ascent of repulsion branch of potential energy well (as obtained from gas properties by means of Lennard-Jones and Devonshire theory)
$N_A$	Avogadro number	$\psi^2$	Charge density (probability of finding an electron) at distance $r$ from the atom nucleus
$r$	Distance from atom nucleus		
$r_0$	Distance between like nonbonded atoms (molecules) at potential energy minimum		
$r_b$	van der Waals radius estimated by Pauling's approximation, $r_b = b + \text{const.}$		
$r_w'$	van der Waals radius derived from nonbonded contact distance in crystals		
$r_w$	van der Waals radius		
$\bar{r}_w$	Mean van der Waals radius for volume calculations involving anisometric atoms		
$V_0$	Molal volume		

### Purpose and Scope

The primary purpose of the present investigation is the calculation of the volume occupied by a molecule, *i.e.*, impenetrable for other molecules with thermal energies at ordinary temperatures. This volume, called here the van der Waals volume ( $V_w$ ), is to serve

as reducing parameter in the study of the physical properties of condensed phases.<sup>1,2</sup> The calculation of  $V_w$  assumes a knowledge of bond distances, bond angles, and the contact distances [*i.e.*, intermolecular van der Waals radii ( $r_w$ )] and shapes characteristic of atoms in various molecular configurations. While most of the important bond distances and angles in organic molecules are reasonably well known and recorded,<sup>3,4</sup> only a few and semiquantitative contact (= nonbonded intermolecular) distances in crystals have been collected.

The first task at hand was therefore the collection of contact distances from reliable X-ray diffraction data in the literature. Selection of the "best" values from the resulting mass of data is of necessity an arbitrary procedure, which will be discussed in the body of this paper. Two important approximations have been made which can only be excused by the desire to obtain results now; namely, the contact distances have not been corrected<sup>5</sup> to 0°K. and all atoms have been treated as spheres and sphere segments, although it is well known that many are more nearly pear-shaped. The reason for the first approximation is the absence of data regarding the often anisotropic thermal expansion coefficients of the crystals from which the contact distance data were obtained. Spherical shapes have been assumed because of the absence of generally agreed pear shapes for the various atoms and the mathematical complexity of testing various alternative shapes for internal consistency. The values of  $V_w$  presented in this paper are therefore subject to further improvement. However, they have proven sufficiently useful, even in their present state, so that their publication appears justified.

### General Principles

Assumption of the existence of a defined spatial extent of atoms is common to kinetic gas theory and X-ray crystallography. The extent of agreement between the dimensions of the rare gas atoms produced by both approaches can be considered as a measure of the status of kinetic gas theory.<sup>6</sup> However, this test is restricted to the rare gases because the crystals of metals, the only other monatomic species, are held together by covalent bonds and therefore do not permit comparison of the interatomic distances during thermal collisions of gas atoms with those prevailing in the solid.

This observation brings us to one of the tacit assumptions of this inquiry, the invariance of the van der Waals radius of an atom under the most drastic environmental changes, *i.e.*, irrespective of its chemical combination and of its nearest nonbonded neighbors

as well as of the phase state in which it is found. Closer examination shows that this assumption is surprisingly valid for heavy atoms, but is not very good with atoms containing only a few electrons, such as hydrogen, fluorine, etc. It may, therefore, be worthwhile to look at the nature of the van der Waals radius from the point of view of the electron density distribution around an atom.

The electron density  $\psi^2$  at distance  $r$  from the core of a hydrogenic one-electron atom is given by the well known relation

$$\psi^2 = C^2 \exp\left(-\frac{2\sqrt{2m_e I_0}}{\hbar} r\right) \quad (1)$$

where  $m_e$  is the rest mass of the electron,  $I_0$  the first ionization potential of the atom, and  $C$  is a normalization constant chosen such that  $\int \psi^2 d\omega = 1$  when the integration is carried out over the whole of space ( $\omega$ ). The shape of the electron density distribution for typical one and multielectron atoms is shown on Fig. 1. As two atoms approach each other from  $r = \infty$  their electron clouds interpenetrate more and more. The Pauli exclusion principle then causes a repulsion<sup>7</sup> of the two atoms in direct proportion<sup>8</sup> to the electron density in the region of interpenetration. One might define the van der Waals radius in terms of that distance  $r$  at which this repulsion just balances the attraction forces between the two atoms. Comparison of the abscissa of Fig. 1 with the empirically known van der Waals radii shows that this distance corresponds to a very low electron density—so low, in fact, that one cannot formulate a "critical" electron density and hope to calculate  $r_w$  from it because of the low degree of accuracy of the known calculating schemes in that part of the energy spectrum.

However, eq. 1 contains a parameter  $\hbar/\sqrt{m_e I_0}$ , the de Broglie wave length  $\lambda_B$  of the outermost valence

(1) A. Bondi, *A.I.Ch.E. J.*, **8**, 610 (1962).

(2) A. Bondi and D. J. Simkin, *ibid.*, **6**, 191 (1960).

(3) Landolt-Bornstein, "Zahlenwerte und Funktionen I/4: Kristalle," Springer, Berlin, 1955.

(4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942, p. 192.

(5) Since the volume increase of most solids between 0°K. and the melting point is about 10%, the van der Waals radii at 0°K. differ from those given here, probably by less than 3%.

(6) J. O. Hirschfelder and R. B. Bird, "Molecular Theory of Gases and Liquids," New York, N. Y., 1959.

(7) See J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., Amsterdam, 1953, p. 146 ff. for a more detailed discussion; a somewhat different treatment is presented by K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, p. 201.

(8) The repulsion potential  $E_{r2} \sim \exp(r/\alpha)$ ; hence, at the distances of the order  $r_w$ , considering eq. 1,  $E_r \sim \psi^2$ , the electron density in the region of interpenetration.

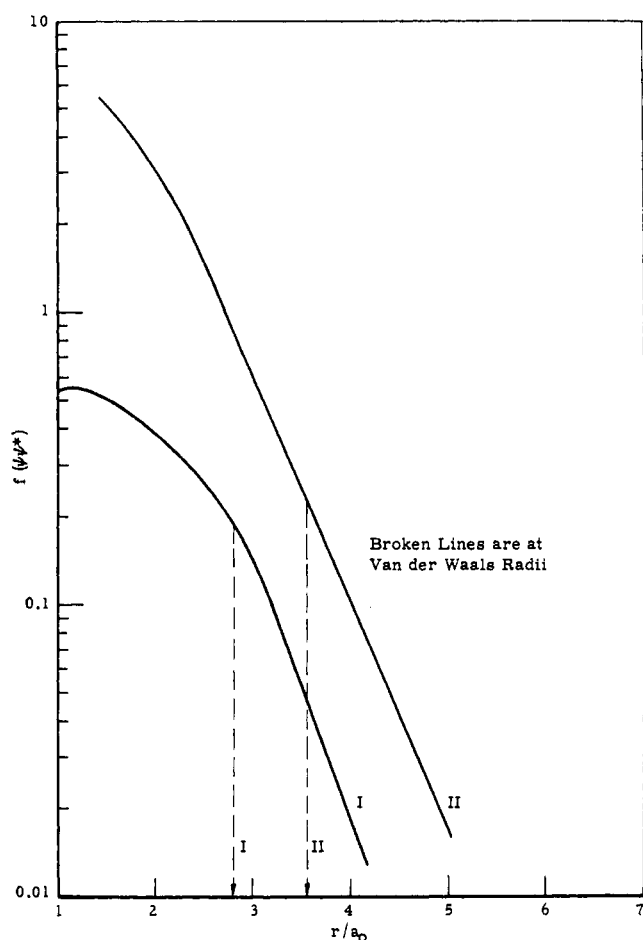


Figure 1. Electron density distribution near the atom "surface," for hydrogen (I) and argon (II) [D. R. and W. Hartree, *Proc. Roy. Soc. (London)*, **A166**, 450 (1938)].

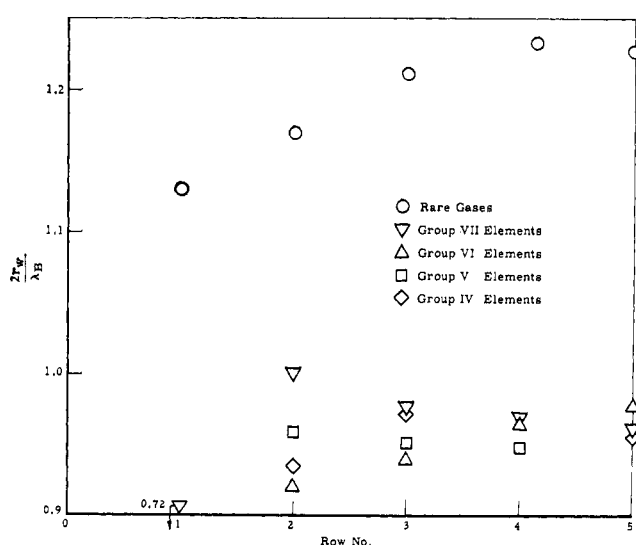


Figure 2. Relation of  $r_w$  (single bond value) to de Broglie wave length  $\lambda_B$  of outer valence electron for nonmetallic elements.

electron of an atom, which might be related to the van der Waals radius ( $r_w$ ). A few years ago Morrison<sup>9</sup> suggested that perhaps  $r_w = (\text{const.}) \lambda_B$ . Our examination of this suggestion brought to light that this simple correlation holds surprisingly well. One finds that the constant is 0.61 for the rare gas atoms, and is—as one might expect—appreciably smaller for bound atoms, *ca.* 0.53 for the halogens and about 0.48 for the remainder of the nonmetallic elements. Deviations from this correlation (shown in Fig. 2) are in the direction of predicting too large a diameter for the lightest elements. As the valence electrons of a covalently bound atom are concentrated between it and its bound neighbor to a degree that depends on the nature of the bond, it is surprising that  $r_w$  retains enough individuality to be correlatable in terms of the ionization potential of the free atom.

Table I: Comparison of Correlation with "Observed" Mean van der Waals Radii (in Å.)

					H	He
$r_b^a$					1.06	..
$\lambda_B/2^b$					1.67	1.24
$\bar{r}_w^c$					1.20	1.40
	B	C	N	O	F	Ne
$r_b$	1.65	1.53	1.46	1.42	1.40	..
$\lambda_B/2$	2.13	1.82	1.61	1.66	1.47	1.32
$\bar{r}_w$	..	1.70	1.55	1.52	1.47	1.54
	Al	Si	P	S	Cl	Ar
$r_b$	..	1.93	1.86	1.80	(1.75) <sup>d</sup>	..
$\lambda_B/2$	2.51	2.15	1.87	1.91	1.70	1.55
$\bar{r}_w$	..	2.10	1.80	1.80	1.75	1.88
	Ga	Ge	As	Se	Br	Kr
$r_b$	..	1.98	1.94	1.90	1.87	..
$\lambda_B/2$	2.51	2.19	1.96	1.97	1.79	1.64
$\bar{r}_w$	..	..	1.85	1.90	1.85	2.02
	In	Sn	Sb	Te	I	Xe
$r_b$	..	2.16	2.12	2.08	2.04	2.05
$\lambda_B/2$	2.55	2.27	2.09	2.05	1.90	1.76
$\bar{r}_w$	..	..	..	2.06	1.98	2.16

<sup>a</sup>  $r_b \equiv b + 0.76$ . <sup>b</sup>  $\lambda_B \equiv 6.13 \times 10^{-8}/\sqrt{I}$ . <sup>c</sup> Only the most frequently used values for single bonded forms of the elements are quoted here. <sup>d</sup> Reference point chosen for the system  $r_b = b + \text{constant}$ .

### Compatibility with Physical Properties

The range of numerical values of  $r_w$  for a given atom obtained from X-ray crystallographic contact distances is usually too wide for the direct application to a meaningful calculation of  $r_w$ . The "best" value of  $r_w$  must

(9) J. D. Morrison, *Rev. Pure Appl. Chem.*, **5**, 46 (1955).

then be obtained by appeal to extraneous information. In the ideal case enough crystal structure and zero point density data are available to fix through calculation that value of  $r_w$  which yields the correct packing density  $\rho_0^*$  at 0°K. This has been done for the simple tetrahalides by Sackmann.<sup>10</sup>

In general, when a detailed analysis is either too laborious or not possible, the "plausibility" of the packing density calculated from the experimental zero point volume<sup>11</sup> and  $V_w$  will fix at least the upper limit of  $r_w$ . The empirical observation that for molecular crystals  $\rho_0^*$  always  $>0.6$  may be used to fix a lower limit on  $V_w$ . The method used to estimate  $V_w$  from bond distance  $l$  and from  $r_w$  is shown on Fig. 3.

A lower limit is set for  $r_w$  by the requirement that the packing density at the critical temperature must be sufficiently high to permit the existence of a continuous three-dimensional network, *i.e.*, the number of nearest neighbors  $Z \geq 3$ .<sup>12</sup> A related criterium is the compatibility with the size of the equivalent sphere obtained by application of kinetic gas theory.<sup>13</sup> The somewhat surprising regularity that  $V_w \approx N_A(\pi/6)\sigma^3$  which we observed whenever  $r_w$  met the other two criteria, is useful when neither  $\rho_0$  nor  $\rho_c$  but only gas properties have been measured.

A particularly arbitrary criterium developed in the course of the present work is that the number of external degrees of freedom of rigid (nonlinear) poly-

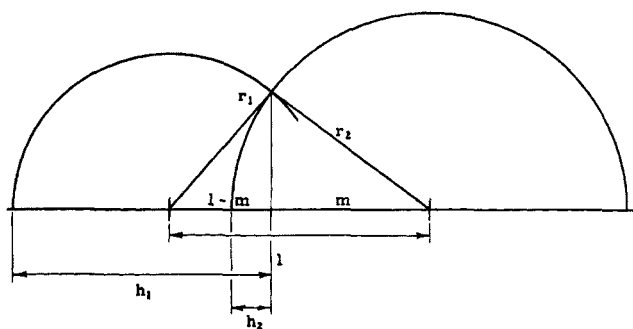
atomic molecules calculated from liquid density and energy of vaporization ( $E^\circ$ ) data, as  $0.391E^\circ/RT \cdot (1.8) = 6 \pm 0.2$ .<sup>2</sup> The application of this criterium requires the availability of good liquid density and vapor pressure or calorimetric heat of vaporization data and great faith in the form of the corresponding states principle adopted for this purpose.

### Experimental Data for Nonmetallic Elements

In this account the long form of the periodic table is followed from right to left.

*The Halides. Fluorine.* The data of Table II show that Pauling's suggestion to set the ionic radius (1.35 Å.) =  $r_w$  yields rather improbable values for  $\rho_0^*$  of well studied fluorine compounds. Crystallographic data for  $\text{NH}_3 \cdot \text{BF}_3$ ,<sup>14</sup>  $\text{SiF}_4$ ,<sup>3,15</sup> phosphonitrilic fluoride,<sup>16</sup> and Teflon<sup>17,18</sup> yield  $r_w(\text{F}) = 1.50$  Å., a value which, according to Table II, is compatible with  $\rho_0$ ,  $\rho_c$ , and  $\sigma$ . The liquid state criterium led to the very similar value  $r_w(\text{F}) = 1.47$  Å. for perfluoroalkanes, aryl fluorides, and for secondary and tertiary alkane fluorides. However, for primary alkane fluorides  $r_w(\text{F}) = 1.40$  Å. was found more compatible with the data. In view of the exactly opposite trend of the C-F bond length, this is an unexpected result, for which neither conflicting nor confirmatory evidence could be found in X-ray diffraction data.

*Chlorine, Bromine, and Iodine.* The previously mentioned analysis of the crystallographic and density data of the tetrahalides of the group IV elements by Sackmann<sup>10</sup> yielded  $r_w(\text{Cl}) = 1.76$  Å.,  $r_w(\text{Br}) = 1.85$  Å.,  $r_w(\text{I}) = 1.96$  Å., in good agreement with many other X-ray diffraction data, shown in Table III. The data of Table IV indicate that the resulting values of  $V_w$  for various halogen compounds are more compatible with experimental density data than are the frequently quoted van der Waals radii based on Pauling's approximation  $r_w = r_i$ . The radii and volume increments derived from the liquid state criteria have been assembled in Table IV. They all show the same value for the primary alkanes previously noted for fluorine.



$r_1, r_2$  = van der Waals radii  
 $l$  = covalent bond distance  
 $m$  = auxiliary parameter  
 $h_1, h_2$  = height of sphere segments  
 $m = \frac{r_2^2 - r_1^2 + l^2}{2l}$ ;  $h_1 = r_1 + l - m$ ;  $h_2 = r_2 - m$   
 $V_1 = \pi h_1^2 (r_1 - \frac{h_1}{3})$ ;  $\Delta V_{2-1} = \pi h_2^2 (r_2 - \frac{h_2}{3})$ ;  $V_2 = \frac{4\pi}{3} r_2^3$

Example:  
van der Waals volume of diatomic molecule:

$V_w = N_A [V_1 + V_2 - \Delta V_{2-1}] \text{ cm}^3/\text{mole}$   
 where  $N_A = 6.02 \times 10^{23}$  molecules/mole  
 and  $r$ 's are given in Angstrom units

Volume of center atom = Total volume of atom  
 Surface area =  $2\pi rh$

Figure 3. Method of calculation.

(10) H. Sackmann, *Z. physik. Chem.*, **208**, 235 (1958).

(11) W. Biltz, "Raumchemie der festen Stoffe," Leipzig, 1934.

(12) This point will be discussed in detail in a subsequent article.

(13) A. Bondi, *J. Phys. Chem.*, **58**, 929 (1954).

(14) J. L. Hoard, *et al.*, *Acta Cryst.*, **4**, 396 (1951).

(15) M. Atoji and W. N. Lipscomb, *ibid.*, **7**, 173 (1954).

(16) H. McGeachin and F. Tromans, *J. Chem. Soc.*, 4777 (1961).

(17) C. W. Bunn and E. R. Howells, *Nature*, **174**, 548 (1954).

(18) H. G. Killiam and E. Jenckel, *Z. Elektrochem.*, **63**, 308 (1959).

**Table II:** Compatibility of Proposed van der Waals Radii of Fluorine with Physical Properties

Sub- stance	$r_w(\text{F})$ , Å.	$V_w$ , cm. <sup>3</sup> /mole	$\frac{V_w}{N_A(\pi/6)\sigma^3}$ <sup>a</sup>	$\rho_0^{*b,c}$	$\rho_0^{*d}$
F <sub>2</sub>	1.35	10.5	0.88	0.42	...
	1.50	14.2	1.19	0.57	...
CF <sub>4</sub>	1.35	16.5	0.51	0.56	0.161
	1.50	29.5	0.92	0.69 <sub>5</sub>	0.200
n-C <sub>7</sub> F <sub>16</sub>	1.35	105.8	..	...	0.160
	1.50	127.7	..	...	0.193

<sup>a</sup> See ref. 6. <sup>b</sup> See ref. 11. <sup>c</sup> G. A. Miller and R. B. Bernstein, *J. Phys. Chem.*, **63**, 710 (1959). <sup>d</sup> K. A. Kobe and R. E. Lynn, *Chem. Rev.*, **52**, 121 (1953), and Miller and Bernstein, preceding reference.

**Table III:** Recent Intermolecular Contact Radii  $r'$  for Chlorine, Bromine, and Iodine in Molecular Crystals

Compound	$r_w'(X)$ , Å.
$\lambda$ -C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub> (Gammexane)	(Cl) 1.70 <sup>a</sup>
Perchlorofulvalene	(Cl) 1.74 <sup>b</sup>
Tetrachloro- <i>p</i> -benzoquinone	(Cl) 1.78 <sup>c</sup>
1,3,5-Trichlorobenzene (90°K.), 293°K.	(Cl) (1.77), 1.82 <sup>d</sup>
1,4-Dibromocyclo[3.2.2]azine	(Br) 1.80 <sup>e</sup>
<i>p</i> -Dibromobenzene	(Br) 1.88 <sup>f</sup>
1,3,5-Tribromobenzene	(Br) 1.88 <sup>d</sup>
Iodoform, 0°K.	1.99 <sup>g</sup>
Phosphorus thiodide	1.95 <sup>h</sup>
<i>p</i> -Diiodobenzene	2.07 <sup>i</sup>

<sup>a</sup> G. W. Van Vlater, *et al.*, *Acta Cryst.*, **3**, 139 (1950). <sup>b</sup> See ref. 21. <sup>c</sup> S. Chu, *et al.*, *Acta Cryst.*, **15**, 661 (1962). <sup>d</sup> H. J. Milledge and L. M. Pant, *ibid.*, **13**, 285 (1960). <sup>e</sup> A. Hanson, *ibid.*, **14**, 124 (1961). <sup>f</sup> U. Croatto, *et al.*, *ibid.*, **5**, 825 (1952). <sup>g</sup> See ref. 30. <sup>h</sup> D. A. Wright and B. R. Penfold, *Acta Cryst.*, **12**, 455 (1959). <sup>i</sup> S. B. Hendricks, *et al.*, *J. Chem. Phys.*, **1**, 549 (1933).

*Oxygen, Sulfur, Selenium, and Tellurium.* As the diameter of singly bonded oxygen and sulfur is smaller than that of methylene or other functional groups to which they might be attached, one finds only few good contact distance data for them. Moreover, in the present context all contacts involving hydrogen bonds must be excluded. As a consequence of being too deeply "buried" within the molecule for frequent (or any) collision with neighboring molecules, the "effective volume" occupied by an ether oxygen atom differs from molecule to molecule. The upper limit on  $r_w(>\text{O})$  set by the few available X-ray data (Table VI), 1.52 Å., corresponds to  $V_w(>\text{O}) = 5.5$  cm.<sup>3</sup>/mole. Only in ethylene oxide is the ether oxygen sufficiently

**Table IV:** Compatibility of Proposed van der Waals Radii of Cl, Br, and I with Physical Properties

Sub- stance	$r_w(X)$ , Å.	$V_w$ , cm. <sup>3</sup> /mole	$\frac{V_w}{N_A(\pi/6)\sigma^3}$ <sup>a</sup>	$\rho_0^{*b}$	$\rho_0^{*c}$
Cl <sub>2</sub>	1.75	24.1	1.09	0.74	0.195
Br <sub>2</sub>	1.85	28.9	1.16	0.75	0.200
	2.00	35.6	1.42	0.93	0.240
I <sub>2</sub>	1.96	37.6	0.96	0.76	...
	2.16	46.0	1.17	0.93	...
CCl <sub>4</sub>	1.75	51.4 <sup>d</sup>	0.8 <sup>e</sup>	0.69	0.186
CBr <sub>4</sub>	1.85	60.8 <sup>d</sup>	0.84	0.69	...
CI <sub>4</sub>	1.97	74.9 <sup>d</sup>	..	0.68	...

<sup>a</sup> See ref. 6 and R. A. Svela, NASA Technical Report R-132 (1962). <sup>b</sup> See ref. 11. <sup>c</sup> See ref. d in Table II. <sup>d</sup> No allowance has been made for possible volume reduction due to overlap of the halogen atoms or for their probable pear shape. Such correction would reduce  $V_w$  and the other reduced densities, but would leave the constancy in the series unchanged.

**Table V:** Effective van der Waals Radii of Bound Halogen Atoms from Liquid State *p-v-t* Property Calculations

X	Attachment	$r_w(X)$ , Å.
F	Primary alkyl	1.40
	<i>sec</i> , <i>tert</i> , alkyl, perfluorous alkane, phenyl	1.47
Cl	Primary alkyl	1.73
	Vinyl	1.75
	<i>sec</i> , <i>tert</i> , alkyl, polychloroalkyl, phenyl	1.77
Br	Primary alkyl	1.84
	<i>tert</i> , polybromoalkyl	1.85
	Phenyl	1.92
I	Primary alkyl	2.01
	<i>tert</i> , polyiodoalkyl, phenyl	2.06

exposed to yield this value of  $V_w(>\text{O})$ . In alkyl ethers, especially polyethers,  $V_w(>\text{O}) = 3.7$  cm.<sup>3</sup>/mole and in polyphenyl ethers it is 3.2 cm.<sup>3</sup>/mole. These values were obtained by fitting polyether data to the generalized density correlation for liquids.

For single-bonded sulfur, X-ray diffraction data point to  $r_w(>\text{S}) = 1.83$  Å., while 1.80 Å. is compatible with various physical properties (Table VII) and with liquid phase density. For single-bonded selenium, a single set of data<sup>19</sup> yields  $r_w(>\text{Se}) = 1.87$  Å. and for tellurium  $V_w(>\text{Te}) = 2.06$  Å.

The geometry of double-bonded oxygen and sulfur is probably quite anisometric. In the direction parallel

(19) R. E. Mush, *Acta Cryst.*, **5**, 458 (1952).

**Table VI:** Intermolecular Contact Radii for Oxygen<sup>a</sup>

Compound	$r_w'(O)$
Single-bonded (ether) oxygen	
Calcium peroxide	1.46 <sup>a</sup>
1,3,6-Trioxane	~1.5 <sup>b</sup>
Bis(1,3-dioxacyclopentyl)	1.47 <sup>b</sup>
Hydroxy L-proline	1.52 <sup>c</sup>
Double-bonded (carbonyl or nitro) oxygen	
Tetrachloro- <i>p</i> -benzoquinone, parallel arrangement	1.35 <sup>d</sup>
Tetrachloro- <i>p</i> -benzoquinone, vertical arrangement	1.63 <sup>d</sup>
Butyne-2, iron octacarbonyl, parallel arrangement	1.47 <sup>e</sup>
Acrylonitrile iron tetracarbonyl	1.53 <sup>a,f</sup>

<sup>a</sup> Only O...O contact are quoted here. The recommended van der Waals radii also take into account the intermolecular contact distances between oxygen and other atoms. <sup>b</sup> See ref. 3. <sup>c</sup> J. Donohue and K. N. Trueblood, *Acta Cryst.*, **5**, 419 (1952). <sup>d</sup> See ref. c in Table III. <sup>e</sup> A. Hock and O. Mills, *Acta Cryst.*, **14**, 139 (1961). <sup>f</sup> A. Luxmoore and M. Truter, *ibid.*, **15**, 1117 (1962). <sup>g</sup> N. G. Vannenberg, *Progr. Inorg. Chem.*, **4**, 125 (1962).

**Table VII:** Compatibility of van der Waals Radii of Sulfur and Selenium with Physical Properties

Substance	$\bar{r}_w$ , Å.	$V_w$ , cm. <sup>3</sup> /mole	$\frac{V_w}{N_A(\pi/6)\sigma^3}$ <sup>a</sup>	$\rho_s^{*b}$	$\rho_c^{*c}$
H <sub>2</sub> S	1.80 (S<)	18.0	1.21	0.675	0.186
S <sub>8</sub>	1.75 (-S-)	92.0	..	0.766	...
CS <sub>2</sub>	1.75 (S)	31.2	1.09	0.69	0.184
H <sub>2</sub> Se	1.90 (Se<)	20.9	..	0.68	...

<sup>a</sup> See ref. 6. <sup>b</sup> See ref. 11. <sup>c</sup> See ref. c in Table II.

to the double bond, one finds  $r_w(O) = 1.40$  Å. (about 1.39 Å. is the cut-off distance of the neutron diffraction pattern of liquid oxygen,<sup>20</sup> and  $1.43 \pm 0.03$  Å. for similar dimensions in various carbonyl compounds. Normal to the double bond axis, one finds dimensions of the order of 1.6 to 1.7 Å., perhaps characteristic for the diameter of a  $\pi$ -electron cloud. Owing to the uncertainty of the geometry of the  $\pi$ -electron cloud, the arbitrary compromise  $r_w(=O) = 1.50$  Å. was adopted, which is compatible with the density data, as shown in Table VIII, and meets the requirements of the liquid state correlation.

The contact distance involving double-bonded sulfur, as in rhodanin<sup>21</sup> [ $r_w(S) = 1.74$  Å.] is smaller than in single-bonded sulfur. Similarly, the contact distance between sulfur atoms in polysulfides and in crystalline sulfur<sup>22</sup> is comparatively short ( $r_w = 1.76 \pm 0.04$  Å.), probably connected with the pronounced double-bond character of the S-S bond.

**Table VIII:** Compatibility of van der Waals Radius of Double-Bonded Oxygen with Physical Properties

Substance	$\bar{r}_w(O)$ , Å.	$V_w$ , cm. <sup>3</sup> /mole	$\frac{V_w}{N_A(\pi/6)\sigma^3}$ <sup>a</sup>	$\rho_s^{*b}$	$\rho_c^{*c}$
O <sub>2</sub>	1.50	13.0	1.03	0.60	0.167
C=O	1.50	16.2	1.01	0.60	0.174
CO <sub>2</sub>	1.50	19.7	0.98	0.76	0.21

<sup>a</sup> See ref. 6. <sup>b</sup> See ref. 11. <sup>c</sup> See ref. c in Table II.

*Nitrogen, Phosphorus, and Arsenic.* The contact distances in a wide variety of nitrogen compounds, assembled in Table IX, suggest that for single- and double-bonded nitrogen  $r_w(N) = 1.55 \pm 0.04$  Å. Triple-bonded nitrogen, as in N<sub>2</sub> and in cyano groups, appears to be quite anisometric with ( $r_w$ ) = 1.40 Å. parallel to the bond and up to 1.7 Å. in the direction normal to bonds. Again the "effective" value was somewhat arbitrarily set at  $r_w(N) = 1.60$  Å. The data of Table X show that the adopted radii for nitrogen are compatible with the density data. They also yield the plausible packing density  $\rho_s^* = 0.706$  for the carefully investigated (tightly packed) crystal of tetracyanoethylene.<sup>23</sup> Smaller values for  $r_w(N)$  would not have given a packing density in keeping with X-ray observations. Further confirmation of the proposed radii comes from the liquid state correlation.

Only very few contact distance data involving phosphorus are available.<sup>16,24</sup> Their average,  $r_w(P) = 1.80$  Å., is of the order expected from the ionization potential and from the covalent bond radius of phosphorus. Only one set of crystallographic data (bromodiphenylarsine) could be found from which  $r_w(As)$  could be estimated as  $\approx 1.85$  Å. This value agrees with the physical property data (Table XI).

*Carbon and Hydrogen.* The available data for the van der Waals radii of carbon in aliphatic and aromatic compounds have been assembled in Table XII. Olefinic carbon is not found in the list because only the so-far unexamined cumulenes, such as allene, could yield the desired contact distances, not being spaced apart by the always larger methyl or functional groups. The data obtained on the various acids and amides on the list could be considered as measures of the width of a double-bonded carbon atom, because the reported spacings are those characteristic of the

(20) D. G. Henshaw, *et al.*, *Phys. Rev.*, **92**, 1229 (1953); **119**, 22 (1960).

(21) P. Wheatley, *J. Chem. Soc.*, 4936 (1961).

(22) J. Donohue in "Organic Sulfur Compounds," N. Kharasch, Ed., New York, N. Y., 1961, p. 1.

(23) D. A. Bekoe and K. N. Trueblood, *Z. Krist.*, **113**, 1 (1960).

(24) E. Kessler and A. Vos, *Acta Cryst.*, **12**, 323 (1959).

**Table IX:** Intermolecular Contact Radii for Nitrogen<sup>a</sup>

Compound	$r_w'(N)$ , Å.
Single-bonded	
Xanthazol	1.48 <sup>b</sup>
S <sub>4</sub> N <sub>4</sub> H <sub>4</sub>	1.58 <sup>c</sup>
Double-bonded	
4-Methylimidazole	1.50 <sup>d</sup>
Glyoxime	1.50 <sup>e</sup>
Guanine	1.54 <sup>f</sup>
Pyrimidine	1.56 <sup>g</sup>
Adenine hydrochloride	1.58 <sup>f</sup>
Diazoaminobenzene copper	1.68 <sup>h</sup>
Tetrazole	1.63 <sup>i,j</sup>
Triple-bonded	
Tetracyanoethylene (N...N contact, normal to bond)	1.70 <sup>k</sup>
Tetracyanoethylene (N...C contact, parallel with bond)	1.39 <sup>k</sup>

<sup>a</sup> Only N...N contacts are quoted here, except where noted otherwise. The recommended van der Waals radii also take into account the intermolecular contact distances between nitrogen and other atoms. <sup>b</sup> W. Nowacki and H. Burki, *Z. Krist.*, **106**, 339 (1955). <sup>c</sup> R. L. Sass and J. Donohue, *Acta Cryst.*, **11**, 497 (1958). <sup>d</sup> H. Zimmerman, *Ann.*, **612**, 193 (1958). <sup>e</sup> W. Hamilton, *Acta Cryst.*, **14**, 95 (1961). <sup>f</sup> J. M. Broomhead, *ibid.*, **1**, 324 (1948); **4**, 92 (1951). <sup>g</sup> N. E. White and C. J. B. Clews, *ibid.*, **9**, 586 (1956). <sup>h</sup> J. H. Bryden, *ibid.*, **8**, 211 (1955). <sup>i</sup> R. N. Brown, *ibid.*, **9**, 163 (1956). <sup>j</sup> Y. D. Kondenshev, *Soviet Phys. Cryst.*, **6**, 413 (1962). <sup>k</sup> See ref. 23.

**Table X:** Compatibility of van der Waals Radii of Nitrogen with Physical Properties of Its Compounds

Substance	$r_w(N)$ , Å.	$V_w$ , cm. <sup>3</sup> /mole	$\frac{V_w}{N_A(\pi/6)\sigma^3}$ <sup>a</sup>	$\rho_0^{*b}$	$\rho_0^{*c}$
N≡N	1.60	15.8	1.01	0.59 <sup>d</sup>	0.176
(C≡N) <sub>2</sub>	1.60	29.4	1.10	...	...
N=O	1.55	13.9	1.07	0.73	...
N=N=O	1.55	18.9	1.03	0.70	0.196
NH <sub>3</sub>	1.55	13.8	...	0.70	0.190

<sup>a</sup> See ref. 6. <sup>b</sup> See ref. 11. <sup>c</sup> See ref. c in Table II. <sup>d</sup> L. H. Bolz, *et al.*, *Acta Cryst.*, **12**, 247 (1959).

**Table XI:** Compatibility of van der Waals Radii of Phosphorus and Arsenic with Physical Properties of Their Compounds

Substance	$r_w(X)$ , Å.	$V_w$ , cm. <sup>3</sup> /mole	$\frac{V_w}{N_A(\pi/6)\sigma^3}$ <sup>a</sup>	$\rho_0^{*b}$	$\rho_0^{*c}$
P <sub>4</sub>	1.80	41.6	(0.81)	0.676	...
PH <sub>3</sub>	1.80	19.7	0.986	0.55	0.174
AsH <sub>3</sub>	1.85	21.3	1.00	0.56	...

<sup>a</sup> See ref. 6. <sup>b</sup> See ref. 11. <sup>c</sup> See ref. c in Table II.

carboxylic carbonyl group. The single datum for the radius of the acetylenic triple bond is supported by the volume data in Table XIII.

**Table XII:** Observed Contact Radii of Carbon and Hydrogen

Aliphatic compounds	$r_w'(C)$ , Å.	$r_w(H)$ , Å.	Ref.
1,3-Dimethyliminotetrazole·HCl	1.66	...	a
Uracil	1.67	...	b
Sodium tropolonate	1.67	...	c
Octatriyne	1.69 <sup>d</sup>	...	e
Succinamide	1.69; 1.70	...	f
Isocyanic acid	1.70	...	g
Succinamic acid	1.70	...	h
n-Triacontane at 0°K.	...	1.17	
n-Hexatriacontane	...	1.18	i
Triethylenediaminenickel(II)			
nitrate	...	1.18	j
Potassium methylene disulfonate	...	1.17	k
Acetylenic triple bonds			
Carbides of Ca, Ba, and Sr	1.78	...	l
Aromatic ring systems			
Coronene	1.72	...	m
Ovalene, perylene	1.75	...	n
Anthraquinone	1.77	...	o
Naphthalene	1.77	1.01	p
Anthracene	1.77	1.01	q
Graphite	1.78	...	r
Dibenzocoronene	1.80	...	s
Benzene	...	1.01; 1.05	t
Pyridine·BF <sub>3</sub>	...	1.0	u

<sup>a</sup> See ref. h in Table IX. <sup>b</sup> G. S. Parry, *Acta Cryst.*, **7**, 313 (1954). <sup>c</sup> R. Shiono, *ibid.*, **14**, 42 (1961). <sup>d</sup> Head-on approach of methyl groups. <sup>e</sup> See ref. 3. <sup>f</sup> R. A. Pasternak, *Acta Cryst.*, **6**, 808 (1953); **9**, 334 (1946). <sup>g</sup> See ref. 3. <sup>h</sup> R. A. Pasternak, *Acta Cryst.*, **7**, 225 (1954). <sup>i</sup> P. W. Teare, *ibid.*, **12**, 294 (1959). <sup>j</sup> L. Swink and M. Atoji, *ibid.*, **13**, 639 (1960). <sup>k</sup> M. Truter, *J. Chem. Soc.*, 3393 (1962). <sup>l</sup> M. Atoji and R. C. Medrud, *J. Chem. Phys.*, **31**, 332 (1959). <sup>m</sup> J. M. Robertson, *et al.*, *J. Chem. Soc.*, 925 (1956). <sup>n</sup> See ref. 28. <sup>o</sup> S. N. Sen, *Indian J. Phys.*, **22**, 347 (1948). <sup>p</sup> D. W. T. Cruikshank, *Acta Cryst.*, **10**, 504 (1957). <sup>q</sup> D. W. T. Cruikshank, *ibid.*, **9**, 915 (1956). <sup>r</sup> J. A. Ibers, private communication. <sup>s</sup> See ref. 29. <sup>t</sup> E. G. Cox, *Rev. Mod. Phys.*, **30**, 159 (1958). <sup>u</sup> S. V. Svenkova, *Kristallografiya*, **2**, 408 (1957).

The head-on approach of the methyl groups on octatriyne provides the most direct measure of the dimensions of an aliphatic carbon atom. However, adoption of  $r_w(C) = 1.69$  Å. would have inspired a false sense of precision regarding this central factor in the entire scheme of volume calculations. Hence  $r_w(C_{\text{aliph}}) = 1.70$  Å. is, in agreement with Briegleb<sup>25</sup> and others,<sup>26</sup> the preferred choice at present.

**Table XIII:** Compatibility of van der Waals Radii of Carbon and Hydrogen with Physical Properties of Simple Hydrocarbons

Substance	$r_w(\text{C})$ , Å.	$r_w(\text{H})$ , Å.	$V_w$ , cm. <sup>3</sup> /mole	$\frac{V_w}{N_A(\pi/6)\sigma^3}$	$\rho_0^{*b}$	$\rho_c^{*c}$
Methane	1.70	1.20	17.1	1.00	0.67	0.173
Ethane	1.70	1.20	27.3	1.00	0.684	0.184
Ethylene	1.70	1.20	23.9	1.00	0.67	0.193
Acetylene	1.78	1.20	23.1	0.98		0.204
Benzene	1.77	1.00	48.4	1.04	0.70	0.186

<sup>a</sup> See ref. 6. <sup>b</sup> See ref. 11. <sup>c</sup> See ref. c in Table II.

The van der Waals radius of aromatic carbon atoms is one-half of the contact distance between nonbonded carbon atoms in adjacent ring planes and is distinctly different from the often quoted interplanar distances. A few shorter distances (as low as 3.20 Å.) between ring carbons in neighboring rings disposed at steep angles have been reported<sup>27-29</sup> but have not been given any weight in the final estimate of  $r_w(\text{C}_w)$ . The value  $r_w(\text{C}_w) = 1.77$  Å. has been adopted as being authenticated by the most careful measurements on the list. The supposition is then, that the benzene ring has a slightly bumpy top (like the top of an old Arab house). The smooth  $\pi$ -electron model of Briegleb does not seem entirely compatible with the observed X-ray diffraction patterns of condensed ring systems. However, the difference in volume between the two models is small.

Neither model predicts the density of graphite correctly. Our model yields a density that is about 5% too high and that of the Briegleb model is about 5% too low. The model predicting too high a density is probably more realistic because it means that there is still some space for thermal motion between the graphite planes. From Bridgman's experiments we know that about 5% of graphite volume is squeezed out by compression to about 10,000 atm.

The contact distances of hydrogen are difficult to ascertain. The best authenticated contacts, by Kitaigorodskii's measurements on *n*-paraffins extrapolated to 0°K.<sup>26,30</sup> and also observed in several other crystals lead to  $r_w(\text{H}_{\text{aliph}}) = 1.17$  Å. This is so close to the commonly accepted value of  $r_w(\text{H}_{\text{aliph}}) = 1.20$  Å. that the latter value was retained for the present work. This choice of aliphatic radii is compatible with the shortest observed contact distance of methyl groups, 3.57 Å., in gear-like packing of aliphatic compounds, as well as with densities and gas properties of small hydrocarbon molecules, as shown by the data of Table XIII. The observed hydrogen-hydrogen contact dis-

tances between aromatic rings in the ring plans of several very careful measurements lead uniformly to  $r_w(\text{H}_w) = 1.0$  Å. The choice of aromatic dimensions is also compatible with density data and gas properties, as shown in Table XIII.

**Silicon, Germanium, and Tin.** No crystallographic contact distances were found for these elements in non-metallic and nonionic crystals. Their van der Waals radii must, therefore, be estimated from correlations, either with covalent bond radii or with ionization potentials. The density of pure silicon and of  $\text{SiH}_4$  (liq) as well as  $\rho_0$  [ $\rho_0^*(\text{SiH}_4) = \rho_0^*(\text{CH}_4) = 0.67$ ] are compatible with a van der Waals radius of 2.1 Å.

**Metals (in Nonmetallic Compounds).** The van der Waals radii of metals in metal organic compounds are very difficult to obtain, because in most crystalline compounds observed to date the metal atom is hidden from nonbonded contacts. Two recent measurements yield rather short radii; in diazoaminobenzene-copper(I)<sup>31</sup> a C...Cu contact yields  $r_w(\text{Cu}) = 1.43$  Å., and in methoxy carbonyl mercuric chloride<sup>32</sup> the (non-bonded) Hg...Cl and the Hg...O contacts yield  $r_w(\text{Hg}) = 1.5$  Å. The latter is only slightly smaller than the value for  $r_0$  estimated from gas viscosity measurements of mercury vapor, namely  $r_0/2 = 1.65 \pm 0.03$  Å. and that estimated from the critical volume (by a method to be discussed in another paper),  $r_0/2 = 1.55$  Å. Other radii derived from critical volumes are assembled in Table XI.

Spectroscopic evidence for the cessation of d-shell, i.e., metallic, interaction in dialkyl glyoxime complexes, when steric hindrance forced the metal atoms apart, indicates that for nickel and palladium  $r_w = 1.63$  Å. and for platinum  $r_w = 1.7$  to 1.8 Å.<sup>33</sup> All of the aforementioned metal radii are substantially smaller than predicted from ionization potentials and somewhat larger, but not uniformly larger, than their covalent bond radii. It is not certain, therefore, how best to estimate the van der Waals radii of metals in metal organic compounds.

(25) G. Briegleb, *Fortschr. Chem. Forsch.*, **1**, 642 (1950).

(26) A. I. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1961.

(27) A. O. McIntosh, *et al.*, *J. Chem. Soc.*, 1661 (1954).

(28) J. M. Robertson, *et al.*, *ibid.*, 925 (1956).

(29) J. M. Robertson and J. Trotter, *ibid.*, 1115 (1961).

(30) A. I. Kitaigorodskii and Y. V. Muinkh, *Soviet Phys. Dokl.*, **3**, 707 (1958).

(31) I. Brown and J. Dimitz, *Acta Cryst.*, **14**, 480 (1961).

(32) T. Mak and J. Trotter, *J. Chem. Soc.*, 3243 (1962).

(33) C. R. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, **80**, 3579, 4767 (1958).



**Table XIV:** Radii of Metal Atoms in Nonbonded State, from Critical Volumes<sup>a</sup> (Except where Noted Otherwise)<sup>b</sup> in Å.

Li					
1.82					
Na	Mg				
2.27	1.73				
K	Ni	Cu	Zn	Ga	
2.75	1.63 <sup>c</sup>	1.4 <sup>d</sup>	1.39	1.87	
	Pd	Ag	Cd	In	Sn
	1.63 <sup>c</sup>	1.72	1.58	1.93	2.17
	Pt	Au	Hg	Tl	Pb
	1.75 <sup>c</sup>	1.66	1.55	1.96	2.02
	1.72 <sup>d</sup>				
U					
1.86					

<sup>a</sup> P. J. McGonigal, *J. Phys. Chem.*, **66**, 1686 (1962). <sup>b</sup>  $r_w = \frac{1}{2}((0.66/\pi N_A)V_c)^{1/3} = \frac{1}{2}(0.70 \times 10^{-24}V_c)^{1/3}$ . <sup>c</sup> From ultraviolet spectroscopy<sup>33</sup> of glyoxime complexes. <sup>d</sup> From X-ray diffraction data: Cu (ref. 31) and Pt [see R. E. Rundle and J. H. Sturdivant, *J. Am. Chem. Soc.*, **69**, 1561 (1947)].

### Summary Tables of Group Increments

For the convenience of the user, a number of frequently occurring group increments have been calculated and assembled in Tables XV and XVI. It should be noted that the group increments in Table XVI are correct only for attachment to carbon atoms. The example of ether oxygen illustrates the seriousness of the error due to neglect of this restriction: in certain alkanes  $V_w(-O-)$  = 5.20 cm.<sup>3</sup>/mole and in siloxanes it is 2.7 cm.<sup>3</sup>/mole.

*Corrections for Intramolecular Crowding and for Association Bonding.* The simple model for the calculation of the van der Waals volume  $V_w$  of molecules shown in Fig. 3 is not always adequate.

1. Care must be taken not to cut larger sphere segments off the central atom than it has volume to provide.

2. Neighboring atoms around a three or four valent central atom would interpenetrate if the sphericities of their shells were preserved to the root. Actually, they do not even squeeze each other very hard, as the bound atoms are probably pear-shaped due to the tighter binding of valence electrons halfway between the two radii. Because of insufficient data on dimensions in this region, we ignored the problem in the calculation of  $V_w$ .

3. More important is the crowding effect in saturated ring structures such as cyclohexane. Typical crowding decrements calculated for these are given in Table XVII.

**Table XV:** Group Contributions to the van der Waals Volume and Surface Area of Hydrocarbons<sup>a</sup>


Groups	$V_w$ , cm. <sup>3</sup> /mole	$A_w$ , cm. <sup>2</sup> /mole $\times 10^3$
Alkane		
—C—	3.33	0
—CH	6.78	0.57
>CH <sub>2</sub>	10.23	1.35
—CH <sub>3</sub>	13.67	2.12
CH <sub>4</sub>	17.12	2.90
<i>n</i> -Paraffins	$6.88 + 10.23 N_c$	$1.54 + 1.35 N_c$
Olefinic		
=C=	6.96	..
>C=C<	10.02	0.61
—CH	8.47	1.08
=CH <sub>2</sub>	11.94	1.86
>C=CH <sub>2</sub>	16.95	2.17
>C=CH	13.49	1.39
Acetylenic		
—C≡	8.05	0.98
≡C—H	11.55	1.74
≡C— (in diacetylene)	7.82	..
Aromatic		
>C— (condensation)	4.74	0.21
>C— (alkyl)	5.54	0.30
>C—H	8.06	1.00
Benzene	48.36	6.01
Phenyl	45.84	5.33
Naphthalene	73.97	8.44
Naphthyl	71.45	7.76

<sup>a</sup> See corrections for crowding and vicinal effects on Table XVII.

4. Strong association causes in some cases sufficient deformation of the participating atoms that it has to be taken into consideration in the selection of contact distances and in the calculation of  $V_w$ .

The best known example of such deformation is that of hydrogen-bonded systems where interatomic distances at times decrease by 0.8 Å. below those expected from the usual contact distance data. An example for sharp decreases of  $d_w$  without hydrogen bonding is the short intralayer distance between nonbonded halide atoms in the crystals of Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub>.<sup>34-36</sup> Guided by the principle that one should adopt the smallest observed intermolecular distances as source of  $r_w$  data, one might have been tempted to use these, namely 1.66, 1.67, and 1.77 Å. instead of 1.75,

**Table XVI:** Functional Group Contributions to van der Waals Volumes and Surface Areas, All Attached to Carbon Atoms<sup>a</sup>

Groups	$V_w$ , cm. <sup>3</sup> /mole	$A_w$ , cm. <sup>2</sup> /mole $\times 10^9$
—O— (c.e.) <sup>b</sup>	5.20	0.74
—O— (a.e.) <sup>b</sup>	3.7	0.6
—O— (ph.e.) <sup>b</sup>	3.2	0.54
—OH <sup>c</sup>	8.04	1.46
>C=O <sup>d</sup>	11.70	1.60
—S—	10.8	..
—SH	14.8	..
Nitrogen and phosphorus		
NH <sub>2</sub>	10.54	1.74
>NH	8.08	0.99
—N—	4.33	0.23
—C≡N	14.70	2.19
—NO <sub>2</sub>	16.8	2.55
 —P	10.44	..
Fluorine		
—F (pr)	5.72	1.10
—F (s,t)	6.20	1.18
—F (p)	6.00	1.15
—F (ph)	5.80	1.10
Chlorine		
—Cl (pr) <sup>e</sup>	11.62	1.80
—Cl (s,t,p)	12.24	1.82
—Cl (v)	11.65	1.80
—Cl (ph)	12.0	1.81
Bromine and iodine		
—Br (pr)	14.40	2.08
—Br (s,t,p)	14.60	2.09
—Br (p)	15.12	2.13
—I (pr)	19.18	2.48
—I (s,t,p)	20.35	2.54
—I (ph)	19.64	2.51

<sup>a</sup> See ref. *f* in Table IX. <sup>b</sup> c.e., heterocycloaliphatic ethers; a.e., (poly)alkane ethers; ph.e., (poly)phenyl ethers. <sup>c</sup> Correction for hydrogen bonding, e.g., O...O (2.78 Å): subtract 1.05 cm.<sup>3</sup> mole per hydrogen bond. <sup>d</sup> Corrections to carboxylates and amides in Table XVII. <sup>e</sup> pr, attached to alkane in primary position; s,t, attached to alkane in secondary or tertiary position; p, per- or polyhalide of alkane; v, attached to vinyl group; ph, attached to phenyl ring. <sup>f</sup> Adjusted to yield the requisite number of external degrees of freedom in rigid molecules in the liquid state. The second-order refinements on the halides are due to this constraint.

1.85, and 1.97 Å. as van der Waals radii for Cl, Br, and I, respectively. The very much higher heat of sublimation increment per halide atom observed for these X<sub>2</sub> crystals than for other halogen compounds was an additional warning signal against the adoption of these anomalously small radii.

**Table XVII:** Decrements in van der Waals Volume and Surface Area due to Intramolecular Crowding and Related Effects

Description	$\delta V_w$ , cm. <sup>3</sup> /mole	$\delta A_w$ , cm. <sup>2</sup> /mole $\times 10^9$
Decrement per cyclohexyl and per cyclopentyl ring, free and in transcondensed cyclic naphthenes	1.14	0.57
Decrement per ring in <i>cis</i> -condensed cyclic naphthenes <sup>a</sup>	2.50	1.2
Decrement per methylene ring condensed to benzene <sup>b</sup>	1.66	0.7
Decrement per dioxane ring	1.70	0.7
Decrement per single bond between conjugated double bonds	0.25	..
Decrement per single bond adjacent to carboxyl or amide group	0.22	..

<sup>a</sup> This appears to be the correct decrement to use with the isomer mixtures produced by the hydrogenation of these ring and higher condensed cyclic aromatics. <sup>b</sup> Or other aromatic ring system; examples: tetralin and indane.

While the short distances between halogen molecules are restricted to these molecules and to the crystalline state, X-ray evidence points to the fact that the shorter distance between hydrogen-bonded atoms prevails in the liquid as well as in the crystalline states for molecules containing hydrogen-bonding groups.<sup>37</sup> The corresponding correction of  $V_w$  therefore cannot be neglected. Figure 4 gives the magnitude of these corrections for several typical hydrogen bonds.

*Comparison with Other Work.*<sup>9</sup> A very similar effort to the present one was undertaken by Kitaigorodskii<sup>26</sup> who, among X-ray crystallographers, has been most consistently concerned with the establishment of reliable intermolecular van der Waals radii. The radii proposed by him have been given considerable weight in arriving at recommended values. It is not surprising, therefore, that many of his  $V_w$  increments, shown in Table XVIII, are similar to those of this work.

Two other authors, Edward<sup>38</sup> and Luzkii,<sup>39</sup> have proposed the calculation of  $V_w$  from  $l$  and  $r_w$ .<sup>40</sup> Both made the simplifying assumption that the volume increment of an atom is a function only of its own

(34) R. L. Collin, *Acta Cryst.*, **5**, 431 (1952).

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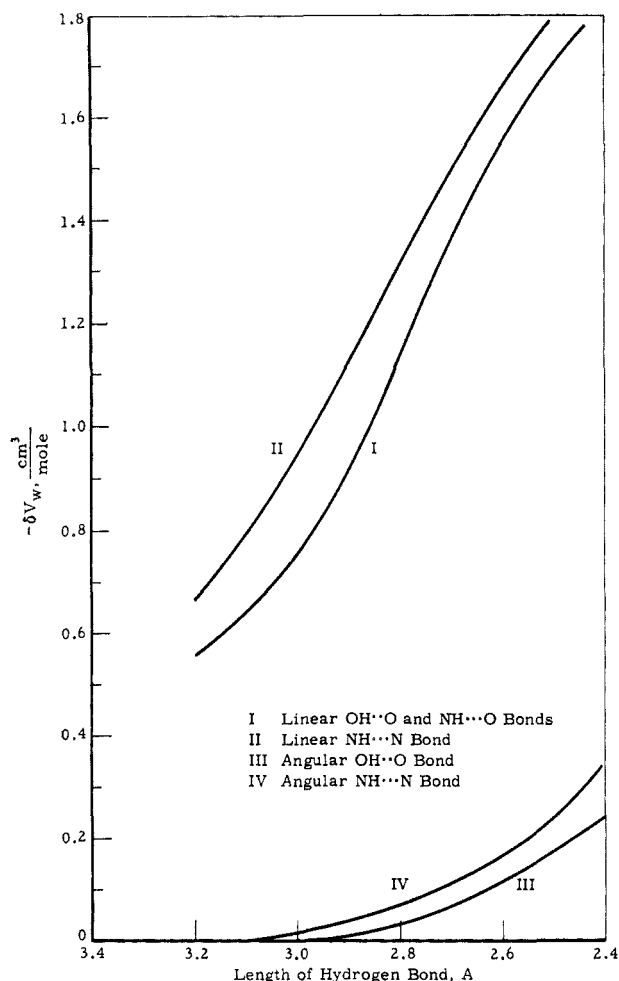


Figure 4. van der Waals volume correction ( $\delta V_w$ ) for hydrogen bond formation.

covalent bond and van der Waals radii and is unaffected by the dimensions of the atom to which it is attached. The errors that can be caused by following this argument have been pointed out earlier in this paper.

The differences between the  $V_w$  increments of these authors and those of the present work, on Table XVIII, are largely due to the use of the old (Pauling) values for  $r_w$ . Edward's high increments for all multiple bond systems is due to his use of Briegleb's model for the  $\pi$ -electron cloud.

Rather interesting is the agreement between the van der Waals volume of various hydrocarbon end groups derived by Hubert and Schultze<sup>41</sup> from the density relations of homologous series and  $V_w$  calculated here, as shown in Table XIX. The adjustment for the more accurate volume of the  $\text{CH}_2$  group (10.23  $\text{cm}^3$ ) instead of that used by Hubert and Schultze

Table XVIII: Comparison of Several Group Increments of  $V_w$  Computed by Different Authors with the Present Work, in  $\text{cm}^3/\text{mole}$

Group	This work	Edward <sup>a</sup>	Kitaigorodskii <sup>b</sup>	Luzkii <sup>c</sup>
$>\text{CH}_2$	10.23	9.90	10.0	8.84
$-\text{CH}_3$	13.67	13.04	13.32	11.61
$-\text{C}-$ (aliph.)	3.33	3.62	3.31	3.30
$\geq\text{C}-$ arom. cond.	4.74	...	4.70	...
$\geq\text{C}-$ arom. alkyl	5.54	...	5.06	4.9
$\geq\text{C}-\text{H}$ arom.	8.06	...	8.37	7.70
$\equiv\text{C}-$	8.05	8.40	...	...
$-\text{F}$	5.72 (aliph.)	5.17	...	...
$-\text{Cl}$	11.62 (aliph.)	12.9	12.78	12.8
$-\text{Br}$	14.40 (aliph.)	16.7	16.6	15.5
$>\text{O}$	5.20	4.51	...	5.77
$=\text{O}$	6.70	7.05	...	6.50
$-\text{N}-$	4.33	4.10	...	4.85
$>\text{S}$	10.8	12.1	...	12.05
$-\text{NO}_2$	11.8	...	13.87	...

<sup>a</sup> See ref. 38. <sup>b</sup> See ref. 26. <sup>c</sup> See ref. 39.

Table XIX: Comparison of  $V_w$  with the Molecular Volume Calculated for End Group Data by Hubert and Schultze<sup>a</sup>

Substance	$V_w$ , $\text{cm}^3/\text{mole}$	$V(\text{H} + \text{S})$ , <sup>b</sup> $\text{cm}^3/\text{mole}$
Ethylene	23.9	25.5
Benzene	48.4	49.2

<sup>a</sup> See ref. 41. <sup>b</sup> Hubert and Schultze's data have been corrected by the factor 10.23/11.1 in order to be consistent with the  $\text{CH}_2$  model of this report.

(11.1  $\text{cm}^3$ ) based on the over-all radius of the  $\text{CH}_2$  group of 2.0 Å. is quite small.

It cannot be overemphasized that the van der Waals radii of this paper have been selected for the calculation of volumes. They may not always be suitable for the calculation of contact distances in crystals.

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