The concordance between the different values in each row of Table III and the close agreement between most of the experimental and calculated values of Table IV show the general applicability of the assumed relationships and constants. The calculated bond energies rarely differ more than 2 or 3 kcal./mole from the experimental values. The larger differences for H_3As, H_2Se and H_2Te are probably due to poor enthalpy data, based on experimental results published in 1888 and earlier. The discrepancies for the simple organic derivatives of sulfur and iodine may be due to error in the assumption that the C–H bond energy is strictly constant. Likewise, the calculation of the N–N bond energy in N_2H_4 on the assumption that the N–H bond energy is the same as in NH_3 is probably unjustified (see Skinner[6]).

ROCHESTER, N. Y.

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Atomic Radii. IV. Dependence of Interatomic Distance on Bond Energy[1]

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It is shown that most of the departures from strict additivity of radii in normal valence compounds can be attributed to variations in bond energy, D_{AB}. A set of "constant energy radii," r_A^*, has been computed. The simple relationship, $r_{AB} = r_A^* + r_B^* - {}^1/_2 \log D_{AB}$, yields interatomic distances which average within 0.02 Å. of the best experimental values. If experimental bond energies are not available, values computed from electronegativities and non-polar bond-energy contributions (see the preceding paper) can be used, with but little loss of accuracy.

Introduction

The hypothesis of constant additive atomic radii was introduced in 1920 by Bragg.[2] Shortly thereafter the writer showed[3] that the Lewis theory of valence was as applicable to crystals as to molecules and ions and pointed out[4] that the valence electron distributions so obtained enable one to predict, in many cases, whether or not constancy and additivity of radii should exist. Various causes of variability were considered in a qualitative manner. It was shown, nevertheless, that a reasonable degree of constancy and additivity exists in certain classes of structures, the essential requirement being that each atom being considered has a sufficiently similar environment in the different substances being compared. Sets of radii for several such classes were computed, the most extensive being a set of *tetrahedral radii*,[5] computed from and for bonds joining atoms, each having a kernel charge $+n$, tetrahedrally to four others, each with a kernel charge of $8 - n$. In 1934, Pauling and Huggins[6] revised and extended these sets of radii and added a set of *normal valence radii*, differing for only six elements from the tetrahedral radii (see Table I).

The writer has consistently pointed out that one should not expect close correspondence between the experimental interatomic distance and the sum of the appropriate radii from the standard set, if the environment of either or both of the atoms differs much from that of the corresponding atom in the class of substances from which the standard radii were derived. Such departures from additivity are, in fact, often found. They are useful in supplying evidence regarding the dependence of the bond length on various factors.

Many of the more marked departures from additivity have been interpreted[7] as resulting from differences in the "degree of double-bond character." On the other hand, Schomaker and Stevenson[8] attribute these departures to varying degrees of bond polarity. They have published a set of *non-polar radii* ($r_{np.A}$) and proposed the following empirical equation for the calculation of single-bond distances from these radii and Pauling's electronegativities[7,9] (x_A)

$$r_{AB} - r_{np.A} + r_{np.B} - 0.09|x_A - x_B| \qquad (1)$$

Although both of these explanations of departures from additivity seem reasonable and can be used to account for the observed distances in a considerable number of instances, Wells[10] has concluded that the sum total of available evidence is against the general applicability of either.

The present paper reports the results of an attempt to correlate interatomic distances with bond energies in a simple manner for single bonds in normal valence elements and compounds.

Theoretical Background

It is theoretically reasonable and experimentally well established that, other things being equal, the greater the bond energy the shorter is the interatomic distance. The bond energy is minus the sum of the repulsion energy and the (negative) attraction energy, when the molecule is in its lowest energy state, *i.e.*, when the interatomic distance is r_{AB}

$$D_{AB} = -E \text{ when } r = r_{AB} \qquad (2)$$

$$E = E_{rep} + E_{att} \qquad (3)$$

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[1] This is a revision of portions of papers presented on Sept. 22, 1949, at the 116th Meeting of the American Chemical Society in Atlantic City and on Sept. 13, 1951, at the XIIth International Congress of Pure and Applied Chemistry in New York, N. Y. For the three previous papers in this series, see references 4, 5 and 6.

[2] W. L. Bragg, *Phil. Mag.*, [6] **40**, 169 (1920).

[3] M. L. Huggins, THIS JOURNAL, **44**, 1841 (1922).

[4] M. L. Huggins, *Phys. Rev.*, **19**, 346 (1922).

[5] M. L. Huggins, *ibid.*, **21**, 205 (1923); **28**, 1086 (1926).

[6] L. Pauling and M. L. Huggins, *Z. Krist.*, **A87**, 205 (1934); quoted in ref. (7).

[7] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

[8] V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

[9] L. Pauling, *ibid.*, **54**, 3570 (1932).

[10] A. F. Wells, *J. Chem. Soc.*, 55 (1949).

TABLE I

ATOMIC RADII

	H[a]	H[b]	H[c]	H[d]	H[e]	C	N	O	F	Si	P	S	Cl
H[5] 1926 Tetrahedral						0.77	0.70	0.65	0.61	1.14	1.08	1.02	0.97
P & H[6] 1934 Tetrahedral						.77	.70	.66	.64	1.17	1.10	1.04	.99
P & H[6] 1934 Normal valence	0.375	0.28	0.28	0.28	0.28	.77	.70	.66	.64	1.17	1.10	1.04	.99
S & S[8] 1941 Non-polar	.37	.37	.37	.37	.37	.77	.74	.74	.72	1.17	1.10	1.04	.99
H 1953 Non-polar ($r_{np,A}$)	.38	.36	.34	.33	.32	.77	.75	.74	.72	1.15	1.11	1.04	1.00
H 1953 Constant energy (r_A^*)	.88	.86	.84	.83	.82	1.22	1.12	1.12	1.11	1.57	1.53	1.46	1.44

	Ge	As	Se	Br	Sn	Sb	Te	I
H[5] 1926 Tetrahedral	1.21	1.16	1.12	1.09	1.36	1.29	1.23	1.19
P & H[6] 1934 Tetrahedral	1.22	1.18	1.14	1.11	1.40	1.36	1.32	1.28
P & H[6] 1934 Normal valence	1.22	1.21	1.17	1.14	1.40	1.41	1.37	1.33
S & S[8] 1941 Non-polar	1.22	1.21	1.17	1.14	1.40	1.41	1.37	1.33
H 1953 Non-polar ($r_{np,A}$)	1.21	1.24	1.17	1.14	1.42	1.45	1.41	1.35
H 1953 Constant energy (r_A^*)	1.61	1.63	1.58	1.56	1.80	1.83	1.79	1.73

[a] In H_2. [b] In bonds with first row elements. [c] In bonds with second row elements. [d] In bonds with third row elements. [e] In bonds with fourth row elements.

The repulsion energy, due primarily to overlapping of the electron clouds of the two atoms concerned, would be expected to vary with the interatomic distance in a manner depending only slightly on the nature and magnitude of the attractions between the atoms. This expectation has been tested and verified for alkali halide crystals by Huggins and Mayer,[11,12] using the exponential repulsion law of Born and Mayer[13]

$$E_{rep} = E^*_{rep} \exp[a(r^*_{AB} - r)] \qquad (4)$$

It was found that (with E^*_{rep} assigned an arbitrary value, the same for all compounds) the constant a in the exponential varies but little from compound to compound and also that, assuming it to be accurately the same in all cases, the *constant energy distances*, r^*_{AB}, can be additively computed from *constant energy radii*, r^*_A, characteristic of the atoms concerned

$$r^*_{AB} = r^*_A + r^*_B \qquad (5)$$

These designations for r^*_{AB} and r^*_A arise from the fact that the former is the distance between atomic centers when the repulsion energy has the constant value D^0_{rep}.

A similar treatment[14,15] has been found satisfactory, at interatomic distances not far from the equilibrium values, for diatomic molecules. Following Morse,[16] an exponential expression was also used for the attraction energy

$$E_{att} = E^e_{att} \exp[a'(r_e - r)] \qquad (6)$$

The constants E^e_{att} and a' do not have the same values for different molecules or for the same molecule in different energy states. For molecules containing only electronegative atoms or hydrogen, a uniform value of a could again be used, and again the r^*_{AB} values computed were found to obey fairly well the additivity relationship (equation (5)).

On assuming equations (3), (4) and (6) and deducing the constants from band spectral data for diatomic molecules, equation (2) is found to be far from accurate. Nevertheless, we shall tentatively assume, as an approximation, that all four of these equations (and also equation (5)) hold for single bonds in normal valence molecules containing only electronegative atoms and hydrogen, with the constants determined by experimental bond-energy and interatomic distance data. We thus have

$$D_{AB} = -E^e_{att} - E^*_{rep} \exp[a(r^*_{AB} - r_e)] \qquad (7)$$

From the equilibrium condition

$$dE/dr = 0 \text{ when } r = r_e \qquad (8)$$

one can deduce

$$-E^e_{att} = \frac{a}{a'} E^*_{rep} \exp[a(r^*_{AB} - r_e)] \qquad (9)$$

Combining equations (7) and (9), we have

$$D_{AB} = \left(\frac{a}{a'} - 1\right) E^*_{rep} \exp[a(r^*_{AB} - r_e)] \qquad (10)$$

We shall assume, for our present purpose, that the first factor in parentheses in this equation is essentially constant. This is equivalent to assuming that the repulsion energy at equilibrium is proportional to the bond energy. The band-spectrum data for diatomic molecules give some justification for this assumption, as a rough approximation. It is less drastic than Morse's hypothesis,[16] that $a = 2a'$. Although essentially an *ad hoc* assumption, the data to be presented will testify as to its general validity. It is possible, nevertheless, that variability of this factor may, in some cases, not be negligible.

Since the value of E^*_{rep} is entirely arbitrary, we shall assume it to have such a value that

$$\left(\frac{a}{a'} - 1\right) E^*_{rep} = 1 \text{ kcal./mole} \qquad (11)$$

Then, replacing r_e by its approximate equivalent, r_{AB}, we have

$$D_{AB} = \exp[a(r^*_{AB} - r_{AB})] \qquad (12)$$

$$r_{AB} = r^*_{AB} - \frac{1}{a} \ln D_{AB} \qquad (13)$$

This equation, combined with the additivity relation (equation (5)), has been tested by application to all available pertinent data. Complete sets of calculations have been made, in which a is taken equal to 4.00, 4.605 and 6.00 × 10^8 cm.$^{-1}$, with less extensive sets for some other values.

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(11) M. L. Huggins and J. E. Mayer, *J. Chem. Phys.*, **1**, 643 (1933).
(12) M. L. Huggins, *ibid.*, **5**, 143 (1937).
(13) M. Born and J. E. Mayer, *Z. Physik*, **75**, 1 (1932).
(14) M. L. Huggins, *J. Chem. Phys.*, **3**, 473 (1935).
(15) M. L. Huggins, *ibid.*, **4**, 308 (1936).
(16) P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).

TABLE II

INTERATOMIC DISTANCES

Bond	r_{AB} calcd. from normal valence radii[6]	r_{AB} calcd. from $D_{np,A}$ and x_A[17]	Molecule or crystal	r_{AB} calcd. from exp. D_{AB}[17]	r_{AB} (exp.)	Source or r_{AB} (exp.)[a]
H–H	0.75	0.751	H_2	0.751	0.749	S^b
H–C	1.07	1.118	CH_4	1.111	1.094	S^c
			C_2H_6		1.102	S^d
H–N	1.00	1.016	NH_3	1.017	1.014	S^c
H–O	0.96	0.963	H_2O	0.958	0.957	S^c
H–F	0.94	0.902	HF	0.906	0.926	S^e
H–Si	1.47	1.461	SiH_4	1.456	1.456	S^c
H–P	1.40	1.426	PH_3	1.428	1 424	S^f
					1.419	M^g
H–S	1.34	1.347	H_2S	1.335	1.334	S^c
H–Cl	1.29	1.276	HCl	1.273	1.284	S^h
H–Ge	1.52	1.505	GeH_4		1.478	S^c
			GeH_3Cl		1.52 ± 0.01	M^i
H–As	1.51	1.534	AsH_3	1.576	1.523	S^f, M^g
H–Se	1.47	1.470	H_2Se	1.500	1.6	S^j
H–Br	1.44	1.418	HBr	1.419	1.423	S^h
H–Sn	1.70	1.694	CH_3SnH_3		1.700 ± 0.015	M^k
H–Sb	1.71	1.729	SbH_3		1.711	S^f
					1.712	M^g
H–Te	1.67	1.690	H_2Te	1.73		
H–I	1.63	1.616	HI	1.623	1.617	S^b
C–C	1.54	1.557	C_2H_6	1.56	1.55 ± 0.03	E^l
					1.543	S^d
			Diamond	1.54	1.541	XC^m
			$C(CH_3)_4$		1.54 ± 0.02	E^l
C–N	1.47	1.489	CH_3NH_2	1.48	1.48	S^c
					1.47 ± 0.01	E^l
			$C_2H_5NH_2$	1.48	1.47 ± 0.02	E^l
			$(CH_3)_2NH$	1.49	1.47 ± 0.02	E^l
					1.46 ± 0.03	E^l
			$(CH_3)_3N$		1.47 ± 0.01	E^l
			$C_6H_{12}N_4$		1.48 ± 0.01	E^l
C–O	1.43	1.435	CH_3OH		1.44 ± 0.01	E^l
			$(CH_3)_2O$	1.42	1.43 ± 0.03	E^l
			CH_3ONO_2		1.43 ± 0.05	E^l
					1.44 ± 0.03	E^l
			CH_3ONO		1.44 ± 0.02	E^l
C–F	1.41	1.365	CF_4	1.355	1.36 ± 0.02	E^l
			CHF_3		1.35 ± 0.03	E^l
					1.34 ± 0.02	E^l
					1.329	S^n
					1.332	M^o
			CH_2F_2		1.32 ± 0.01	S^p
					1.358 ± 0.001	M^q
					1.357 ± 0.017	E^r
			CH_3F		1.398	S^c
					1.42 ± 0.02	E^l
					1.39 ± 0.02	E^l
					1.385	M^s
			$CClF_3$		1.323	M^t
			CCl_2F_2		1.35 ± 0.03	E^l
			CCl_3F		1.40 ± 0.04	E^l
					1.44 ± 0.04	E^l
			$CBrF_3$		1.321	M^u
					1.33 ± 0.015	M^v
			CBr_3F		1.44 ± 0.06	E^l
			CIF_3		1.33 ± 0.015	M^v
			$CHClF_2$		1.36 ± 0.03	E^l
			$CHCl_2F$		1.41 ± 0.03	E^l
			CH_2ClF		1.40 ± 0.03	E^l
C–Si	1.94	1.883	SiC	1.89	1.89	XC^m
			$Si(CH_3)_4$		1.888 ± 0.02	E^w

TABLE II (*Continued*)

Bond	r_{AB} calcd. from normal valence radii[6]	r_{AB} calcd. from $D_{np,A}$ and x_A[17]	Molecule or crystal	r_{AB} calcd. from exp. D_{AB}[17]	r_{AB} (exp.)	Source of r_{AB} (exp.)[a]
			CH_3SiF_3		1.88	M^z
			$(CH_3)_2SiCl_2$		1.83 ± 0.06	E^l
C–P	1.87	1.865	$P(CH_3)_3$		1.87 ± 0.02	E^l
C–S	1.81	1.812	$(CH_3)_2S$	1.83	1.82 ± 0.01	E^l
			$(CH_3)_2S_2$		1.78 ± 0.03	E^l
C–Cl	1.76	1.754	CCl_4	1.749	1.755 ± 0.005	E^l
					1.765 ± 0.015	E^l
					1.761	E^l
					1.77 ± 0.02	E^l
					1.75 ± 0.01	XG^y
			$CHCl_3$	1.75	1.767	M^o
					1.77 ± 0.02	E^l
					1.81	XG^y
			CH_2Cl_2	1.75	1.772	M^z
					1.77 ± 0.02	E^l
			CH_3Cl	1.75	1.77 ± 0.01	E^l
					1.780 ± 0.002	M^{aa}
					1.779	M^{ab}
					1.7810	M^{ac}
			$CClF_3$		1.765	M^t
			CCl_2F_2		1.74 ± 0.03	E^l
			CCl_3F		1.76 ± 0.02	E^l
			$CHCl_2F$		1.73 ± 0.04	E^l
			$CHClF_2$		1.73 ± 0.03	E^l
			CH_2ClF		1.76 ± 0.02	E^l
			CBr_2Cl_2		1.75	E^l
			$CBrCl_3$		1.76	E^l
			$C(CH_3)_3CH_2Cl$		1.74 ± 0.03	E^{ad}
			$Si(CH_3)_3CH_2Cl$		1.73 ± 0.03	E^{ad}
C–Ge	1.99	1.939	$Ge(CH_3)_4$		1.98 ± 0.03	E^l
C–As	1.98	1.983	$As(CH_3)_3$		1.98 ± 0.02	E^l
C–Br	1.91	1.909	CBr_4	1.908	1.91 ± 0.02	E^l
					1.93 ± 0.02	E^l
					1.94 ± 0.02	E^l
					1.942 ± 0.003	E^l
			$CHBr_3$	1.91	1.91	$E^{l,ae}$
					1.930 ± 0.003	M^{af}
			CH_2Br_2	1.91	1.91 ± 0.02	E^l
			CH_3Br	1.91	1.91 ± 0.06	E^l
					1.9391	M^{ac}
			$CBrF_3$		1.936	M^u
					1.91 ± 0.02	M^v
			CBr_3F		1.91 ± 0.04	E^l
			$CBrCl_3$		2.01	E^l
			CBr_2Cl_2		1.93	E^l
C–Sn	2.17	2.140	$Sn(CH_3)_4$		2.18 ± 0.03	E^l
			CH_3SnH_3		2.143 ± 0.002	M^k
			$(CH_3)_3SnCl$		2.19 ± 0.03	E^l
			CH_3SnBr_3		~2.17	E^l
			$(CH_3)_3SnBr$		2.17 ± 0.05	E^l
C–I	2.10	2.114	CI_4		2.12 ± 0.02	E^l
					2.15 ± 0.02	E^l
			CHI_3	2.14	2.12 ± 0.03	E^l
			CH_2I_2	2.15	2.12 ± 0.04	E^l
			CH_3I	2.14	2.132	M^{ab}
					2.1392	M^{ac}
			CF_3I		2.14 ± 0.02	M^v
N–N	1.40	1.487	N_2H_4	1.49	1.47 ± 0.02	E^l
					1.46 ± 0.02	XC^{ag}
			$(CH_3)_2N_2H_2$		1.45 ± 0.03	E^l
			N_4S_4		1.47	E^l
N–O	1.36	1.458	NH_2OH		1.46	S^{ah}
N–F	1.34	1.377	NF_3	1.356	1.37 ± 0.02	E^l

TABLE II (*Continued*)

Bond	r_{AB} calcd. from normal valence radii[6]	r_{AB} calcd. from $D_{np,A}$ and x_A[17]	Molecule or crystal	r_{AB} calcd. from exp. D_{AB}[17]	r_{AB} (exp.)	Source of r_{AB} (exp.)[a]
					1.371	M^{ai}
N–S	1.74	1.750	N_4S_4		1.74	E^{l}
					1.62 ± 0.02	E^{l}
N–Cl	1.69	1.732	NCl_3	1.77		
			$NHCl_2$		1.76	S^{aj}
			CH_3NCl_2		1.74 ± 0.02	E^{l}
			$(CH_3)_2NCl$		1.77 ± 0.02	E^{l}
O–O	1.32	1.474	H_2O_2	1.479	1.47 ± 0.02	E^{l}
					1.49 ± 0.02	XC^{ak}
					1.48	S^{c}
O–F	1.30	1.436	OF_2	1.403	1.41 ± 0.05	E^{l}
					1.38 ± 0.03	S^{al}
			NO_3F		1.42 ± 0.05	E^{l}
O–Si	1.83	1.688	SiO_2	1.68	1.61	XC^{m}
			$Si(OCH_3)_4$		1.64 ± 0.003	E^{am}
			$(CH_3)_6Si_3O_3$		1.66 ± 0.04	E^{an}
			$(CH_3)_3SiOSi(CH_3)_3$		1.63 ± 0.03	E^{am}
			$Cl_3SiOSiCl_3$		1.64 ± 0.05	E^{am}
O–P	1.76	1.688	P_4O_6		1.67 ± 0.03	E^{l}
					1.65 ± 0.02	E^{l}
					1.63	S^{ao}
O–Cl	1.65	1.716	Cl_2O	1.713	1.68 ± 0.03	E^{l}
					1.701 ± 0.020	E^{ap}
O–As	1.87	1.795	As_4O_6	1.816	1.80 ± 0.02	E^{l}
					1.78 ± 0.02	E^{l}
O–Sb	2.07	1.992	Sb_4O_6	1.996	2.0 ± 0.1	XC^{aq}
			Sb_2O_3		2.00	XC^{ar}
F–F	1.28	1.442	F_2	1.438	1.435 ± 0.01	E^{l}
F–Si	1.81	1.614	SiF_4	1.614	1.54 ± 0.02	E^{l}
			$SiHF_3$		1.561 ± 0.005	M^{as}
			SiH_3F		1.593 ± 0.002	M^{at}
			$SiClF_3$		1.560 ± 0.005	M^{as}
			$SiBrF_3$		1.560 ± 0.005	M^{as}
F–P	1.74	1.612	PF_3		1.52 ± 0.04	E^{l}
					1.535	M^{au}
F–Cl	1.63	1.661	ClF	1.661 or 1.657	1.6281	M^{av}
F–Ge	1.86	1.663	GeF_4		1.67 ± 0.03	E^{aw}
F–As	1.85	1.716	AsF_3	1.717	1.72 ± 0.02	E^{l}
					1.712 ± 0.006	S^{ax}
F–Br	1.76	1.774	BrF	1.778	1.759	M^{ay}
F–Sb	2.05	1.912	SbF_3	1.923		
Si–Si	2.34	2.290	Si	2.29	2.352	XC^{az}
			Si_2H_6		2.32 ± 0.03	E^{l}
Si–S	2.21	2.136	SiS_2	2.13	2.14	XC^{m}
Si–Cl	2.16	2.033	$SiCl_4$	2.032	2.02 ± 0.02	E^{l}
			$SiHCl_3$		1.98 ± 0.02	XG^{y}
					2.00 ± 0.03	E^{l}
					2.01 ± 0.03	E^{l}
					2.05 ± 0.03	E^{l}
			SiH_2Cl_2		2.02 ± 0.03	E^{l}
			SiH_3Cl		2.06 ± 0.05	E^{l}
					2.035	M^{ba}
					2.048 ± 0.004	M^{bb}
			$SiClF_3$		1.989 ± 0.018	M^{as}
					2.03 ± 0.03	E^{l}
			$SiBrCl_3$		2.05 ± 0.05	E^{l}
Si–Br	2.31	2.197	$SiBr_4$	2.199	2.14 ± 0.02	E^{l}
					2.15 ± 0.02	E^{l}
			SiH_3Br		2.209	M^{bc}
			$SiBrF_3$		2.153 ± 0.018	M^{as}
			$SiBr_2F_2$		2.16 ± 0.02	E^{l}
Si–I	2.50	2.430	SiI_4	2.436	2.43 ± 0.02	E^{l}

TABLE II (*Continued*)

Bond	r_{AB} calcd. from normal valence radii[6]	r_{AB} calcd. from $D_{np,A}$ and x_A[17]	Molecule or crystal	r_{AB} calcd. from exp. D_{AB}[17]	r_{AB} (exp.)	Source of r_{AB} (exp.)[a]
P–P	2.20	2.210	Normal P_4	2.205	2.21 ± 0.02	E^l
			P (black)		2.17–2.20	XC^m
P–S	2.14	2.121	P_4S_3		2.15	E^l
P–Cl	2.09	2.027	PCl_3	2.023	2.00 ± 0.02	E^l
					2.03 ± 0.02	E^l
					2.043 ± 0.003	M^{bd}
P–Br	2.24	2.191	PBr_3	2.188	2.23 ± 0.01	E^l
					2.18 ± 0.03	E^l
P–I	2.43	2.420	PI_3	2.415	2.52 ± 0.01	E^l
					2.46	E^l
					2.43 ± 0.04	E^l
S–S	2.08	2.070	S_6	2.058		
			S_8	2.053	2.07 ± 0.02	E^l
					2.08 ± 0.02	E^l
			H_2S_2		2.05 ± 0.02	E^l
			S_2Cl_2		2.04 ± 0.05	E^l
					2.05 ± 0.03	E^l
					2.07 ± 0.10	E^l
S–Cl	2.03	2.007	SCl_2		1.99 ± 0.03	E^l
					2.00 ± 0.02	E^l
			S_2Cl_2	2.015	1.98 ± 0.05	E^l
					1.99 ± 0.03	E^l
					2.01 ± 0.07	E^l
S–As	2.25	2.241	As_4S_4	2.230	2.23 ± 0.02	E^l
					2.19–2.27	XC^{be}
			As_4S_6	2.230	2.25 ± 0.02	E^l
S–Br	2.18	2.167	S_2Br_2	2.156		
Cl–Cl	1.98	1.998	Cl_2	1.998	1.988	S^{bf}
Cl–Ge	2.21	2.085	$GeCl_4$	2.097	2.08 ± 0.03	E^l
			GeH_3Cl		2.147 ± 0.005	M^i
Cl–As	2.20	2.137	$AsCl_3$	2.138	2.16 ± 0.03	E^l
					2.17 ± 0.02	E^l
					2.161 ± 0.004	M^{bd}
			$(CH_3)_2AsCl$		2.18 ± 0.04	E^l
Cl–Se	2.16	2.137	$SeCl_2$	2.138		
Cl–Br	2.13	2.138	BrCl	2.141	2.138	M^{bg}
Cl–Sn	2.39	2.283	$SnCl_4$	2.296	2.30 ± 0.03	E^l
			CH_3SnCl_3		2.32 ± 0.03	E^l
			$(CH_3)_2SnCl_2$		2.34 ± 0.03	E^l
			$(CH_3)_3SnCl$		2.37 ± 0.03	E^l
Cl–Sb	2.40	2.336	$SbCl_3$	2.334	2.37 ± 0.02	E^l
Cl–Te	2.36	2.331	$TeCl_2$		2.36 ± 0.03	E^l
Cl–I	2.32	2.313	ICl	2.319	2.30 ± 0.03	E^l
					2.324	S^h
Ge–Ge	2.44	2.419	Ge	2.408	2.450	XC^{az}
			Ge_2H_6		2.41 ± 0.02	E^l
Ge–Br	2.36	2.252	$GeBr_4$		2.32	E^l
					2.34	E^l
					2.29 ± 0.02	E^l
Ge–I	2.55	2.490	GeI_4	2.470	2.47	E^l
					2.48	E^l
					2.50 ± 0.03	E^l
As–As	2.42	2.470	Normal As_4	2.470	2.44 ± 0.03	E^l
As–Br	2.35	2.306	$AsBr_3$	2.308	2.36 ± 0.02	E^l
					2.31	E^l
					2.33 ± 0.02	E^l
			$(CH_3)_2AsBr$		2.34 ± 0.04	E^l
As–I	2.54	2.543	AsI_3	2.547	2.58 ± 0.01	E^l
					2.51	E^l
					2.541	E^l
					2.55 ± 0.03	E^l
			$(CH_3)_2AsI$		2.52 ± 0.03	E^l
Se–Se	2.34	2.348	Se_6		2.32	E^l

TABLE II (*Continued*)

Bond	r_{AB} calcd. from normal valence radii[6]	r_{AB} calcd. from $D_{np,A}$ and x_A[17]	Molecule or crystal	r_{AB} calcd. from exp. D_{AB}[17]	r_{AB} (exp.)	Source of r_{AB} (exp.)[a]
			Se_8		2.34 ± 0.02	XC[bh]
			Se (gray)	2.32	2.32	XC[m]
Br–Br	2.28	2.289	Br_2	2.288	2.28 ± 0.02	E[l]
					2.279	E[l]
					2.286	S[h]
Br–Sn	2.54	2.452	$SnBr_4$	2.454	2.44 ± 0.02	E[l]
			CH_3SnBr_3		2.45 ± 0.02	E[l]
			$(CH_3)_2SnBr_2$		2.48 ± 0.02	E[l]
			$(CH_3)_3SnBr$		2.49 ± 0.03	E[l]
Br–Sb	2.55	2.506	$SbBr_3$	2.473	2.52 ± 0.02	E[l]
					2.47	E[l]
					2.51 ± 0.02	E[l]
Br–Te	2.51	2.502	$TeBr_2$		2.49 ± 0.03	E[l]
					2.51 ± 0.02	E[l]
Br–I	2.47	2.478	IBr	2.476		
Sn–Sn	2.80	2.834	Sn (gray)	2.824	2.80	XC[m]
Sn–I	2.73	2.694	SnI_4		2.64 ± 0.04	E[l]
					2.63	XC[m]
			CH_3SnI_3		2.68 ± 0.02	E[l]
			$(CH_3)_2SnI_2$		2.69 ± 0.03	E[l]
			$(CH_3)_3SnI$		2.72 ± 0.03	E[l]
Sb–Sb	2.82	2.894	Normal Sb (cr)	2.888	2.87	XC[m]
Sb–I	2.74	2.747	SbI_3	2.738	2.75 ± 0.02	E[l]
					2.74	E[l]
					2.67 ± 0.03	E[l]
Te–Te	2.74	2.814	Te (cr)		2.86	XC[m]
I–I	2.66	2.694	I_2	2.681	2.66 ± 0.01	E[l]
					2.674	E[l]
					2.662	S[bi]
					2.70	XC[m]

[a] S = from spectroscopic data, usually infrared; M = from microwave data; E = from electron diffraction data from gas; XC = from X-ray diffraction data from crystal; XG = from X-ray diffraction data from gas. [b] H. Sponer, "Molekülspektren. I," J. Springer, Berlin, 1935. [c] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945. [d] G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952). [e] R. M. Talley, H. M. Kaylor and A. H. Nielsen, *Phys. Rev.*, **77**, 529 (1950). [f] H. H. Nielsen, *J. Chem. Phys.*, **20**, 759 (1952). [g] C. C. Loomis and M. W. P. Strandberg, *Phys. Rev.*, **81**, 798 (1951). [h] G. Herzberg, "Molekülspektren und Molekülstruktur. I. Zweiatomige Moleküle," T. Steinkopff, Dresden and Leipzig, 1939. Calculated from r_e. [i] B. P. Dailey, J. M. Mays and C. H. Townes, *Phys. Rev.*, **76**, 472 (1949). [j] D. M. Cameron, W. C. Sears and H. H. Nielsen, *J. Chem. Phys.*, **7**, 994 (1939). [k] D. R. Lide, Jr., *J. Chem. Phys.*, 19, 1605 (1951). [l] P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950). [m] R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948, 1951. [n] H. J. Bernstein and G. Herzberg, *J. Chem. Phys.*, 16, 30 (1948). [o] S. N. Ghosh, R. Trambarulo and W. Gordy, *ibid.*, **20**, 605 (1952). [p] H. B. Stewart and H. H. Nielsen, *Phys. Rev.*, **75**, 640 (1949). [q] D. R. Lide, Jr., THIS JOURNAL, **74**, 3548 (1952). [r] W. C. Hamilton and K. Hedberg, *ibid.*, **74**, 5529 (1952). [s] O. R. Gilliam, H. D. Edwards and W. Gordy, *Phys. Rev.*, **75**, 1014 (1949). [t] D. K. Coles and R. H. Hughes, *ibid.*, **76**, 858 (1949). [u] A. H. Sharbaugh, B. S. Pritchard and T. C. Madison, *ibid.*, **77**, 302 (1950). [v] J. Sheridan and W. Gordy, *J. Chem. Phys.*, **20**, 591 (1952). [w] W. F. Sheehan, Jr., and V. Schomaker, THIS JOURNAL, **74**, 3956 (1952). [x] J. Sheridan and W. Gordy, *Phys. Rev.*, **77**, 719 (1950). [y] M. H. Pirenne, "The Diffraction of X-rays and Electrons by Free Molecules," Cambridge Univ. Press, Cambridge, England, 1946. [z] R. J. Meyers and W. D. Gwinn, quoted by D. R. Lide, Jr.[q] [aa] G. Matlack, G. Glockler, D. R. Bianco and A. Roberts, *J. Chem. Phys.*, 18, 332 (1950). [ab] J. W. Simmons, W. Gordy and A. G. Smith, *Phys. Rev.*, **74**, 1246 (1948). [ac] S. L. Miller, L. C. Aamodt, C. Dousmanis, C. H. Townes and J. Kraitchman, *J. Chem. Phys.*, **20**, 1112 (1952). [ad] J. M. Hastings and S. H. Bauer, *ibid.*, 18, 13 (1950). [ae] S. Kojima, K. Tsukada, S. Hagiwara, M. Mizushima and T. Ito, *ibid.*, **20**, 804 (1952). [af] Q. Williams, J. T. Cox and W. Gordy, *ibid.*, **20**, 1524 (1952). [ag] R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, **4**, 10 (1951). [ah] P. A. Giguère and I. D. Liu, *Canadian J. Chem.*, **30**, 948 (1952). [ai] J. Sheridan and W. Gordy, *Phys. Rev.*, **79**, 513 (1950). [aj] G. E. Moore and R. M. Badger, THIS JOURNAL, **74**, 6076 (1952). [ak] S. C. Abrahams, R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, 4, 15 (1951). [al] H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 685 (1950). [am] K. Yamasaki, A. Kotera, M. Yokoi and Y. Ueda, *ibid.*, 18, 1414 (1950). [an] E. H. Aggarwal and S. H. Bauer, *ibid.*, **18**, 42 (1950). [ao] H. Gerding, *J. chim. phys.*, 46, 118 (1949). [ap] J. D. Dunitz and K. Hedberg, THIS JOURNAL, **72**, 3108 (1950). [aq] K. E. Almin and A. Westgren, *Arkiv. Kemi, Mineral. Geol.*, 15**B**, No. 22 (1942). [ar] M. J. Buerger and S. B. Hendricks, *Z. Krist.*, **98**, 1 (1938). [as] J. Sheridan and W. Gordy, *J. Chem. Phys.*, 19, 965 (1951). [at] A. H. Sharbaugh, V. G. Thomas and B. S. Pritchard, *Phys. Rev.*, **78**, 64 (1950). [au] Q. Williams, J. Sheridan and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952). [av] D. A. Gilbert, A. Roberts and P. A. Griswold, *Phys. Rev.*, **76**, 1723 (1949). [aw] A. D. Caunt, H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 943 (1951). [ax] B. P. Dailey, K. Rusinow, R. G. Shulman and C. H. Townes, *Phys. Rev.*, 74, 1245 (1948). [ay] D. F Smith, M. Tidwell and D. V. P. Williams, *ibid.*, **77**, 420 (1950). [az] M. Straumanis and E. Z. Aka, *J. Applied Phys.*, **23**, 330 (1952). [ba] A. H. Sharbaugh, *Phys. Rev.*, **74**, 1870 (1948). [bb] J. M. Mays and B. P. Dailey, *J. Chem. Phys.*, **20**, 1695 (1952). [bc] A. H. Sharbaugh, J. K. Bragg, T. C. Madison and V. G. Thomas, *ibid.*, **76**, 1419 (1949). [bd] P. Kisliuk and C. H. Townes, *J. Chem. Phys.*, **18**, 1109 (1950). [be] T. Ito, N. Morimoto and R. Sadanaga, *Acta Cryst.*, **5**, 775 (1952). [bf] W. Hume-Rothery, *Proc. Roy. Soc.* (*London*), A**197**, 17 (1949). [bg] D. F. Smith, M. Tidwell and D. V. P. Williams, *Phys. Rev.*, **79**, 1007 (1950). [bh] R. D. Burbank, *Acta Cryst.*, **4**, 140 (1951). [bi] D. H. Rank and W. M. Baldwin, *J. Chem. Phys.*, 19, 1210 (1951).

The general degree of agreement between experimental and calculated interatomic distances is quite insensitive to the choice of *a*, within this range. The constant energy radii and calculated interatomic distances given here are all for a value of

$$a = 4.605 \times 10^8 \text{ cm.}^{-1} \qquad (14)$$

This choice has the advantage of yielding the simple relationship

$$r_{AB} = r^*_A + r^*_B - {}^1/_2 \log D_{AB} \qquad (15)$$

when the values of r_{AB}, r^*_A and r^*_B are in Å. and those of D_{AB} are in kcal./mole.

Comparison with Experiment

With the aid of this equation, the constant energy radii listed in Table I have been obtained. These, in turn, have been used to compute the values of r_{AB} (calcd.) listed and compared with the corresponding experimental values in Table II.

Calculations have been made both from the experimental bond energies and from bond energies computed from electronegativities and non-polar bond-energy contributions. Both of these are given in the preceding paper.[17]

The average differences between the observed and computed distances are about 0.019 Å. for the figures from experimental bond energies and about 0.024 Å. for those from computed bond energies. These averages would be reduced somewhat if one omitted those cases in which, from other considerations, there is reason to believe that the experimental values of the bond energy (*e.g.*, H–As) or the bond length (*e.g.*, H–Se or Te–Te) are quite inaccurate.

In order to obtain even rough agreement for the hydrogen compounds, it was found necessary to use several different values of r^*_H, depending on the row of the Periodic Table in which the element to which the hydrogen is bonded belongs. This is probably a result of the fact, already noted,[15] that these bonds do not obey the assumed energy–distance relationship well, at least with the same value of a which is found satisfactory for other bonds. An alternative explanation is that equation (11) does not hold with sufficient accuracy for bonds involving hydrogen, with the same value of E^*_{rep} as is satisfactory for other bonds.

It will be noted that the discrepancies in the cases of such very strong, very polar bonds as Si–O and Si–F have been greatly reduced, but not entirely eliminated. (A different assumption as to the sublimation energy of silicon does not improve the situation appreciably.) It seems likely that here, as with bonds involving hydrogen, the basic assumptions underlying the present treatment no longer hold with sufficient accuracy. One way out of the difficulty would be to add to equation (15) another term, involving either the electronegativity or perhaps the fraction of double-bond character, but this does not seem warranted in the present state of our knowledge.

Instead of using Equation (15), one can obviously compute interatomic distances from the non-polar radii by means of the relation

$$r_{AB} = r_{np,A} + r_{np,B} - {}^1/_2 \log \left(\frac{D_{AB}}{D_{np,A} + D_{np,B}}\right) \qquad (16)$$

making use of the non-polar bond-energy contributions listed in the preceding paper. A set of non-polar radii, consistent with the constant energy radii and the non-polar bond-energy contributions which have been listed, is included in Table I. The differences between these and the corresponding radii given by Schomaker and Stevenson are slight. Differences between interatomic distances calculated by equation (16) and those calculated by equation (15) are only such as result from rounding off of the atomic constants used.

In summary, the results presented show that interatomic distances for single bonds between atoms exhibiting their normal valences can be computed, at least within about 0.02 Å., from experimental or calculated bond energies by means of equation (15) or (16), and the constant energy radii of Table I.

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[17] M. L. Huggins, THIS JOURNAL, **75**, 4122 (1953).

[CONTRIBUTION FROM THE MASS SPECTROSCOPY LABORATORY, HOWARD UNIVERSITY]

Electron Impact Studies in CH_4, CH_3Cl, CH_3Br and CH_3I

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Data on the appearance potentials of the positive ions produced on electron impact with CH_4, CH_3Cl, CH_3Br and CH_3I in a 60° Nier type mass spectrometer are used to calculate the heat of sublimation of carbon, $L(C) \leq 5.90$ e.v. Further calculations from the data give $D(C\text{–}H) = 3.5$ e.v., $D(C\text{–}2H) \leq 7.4$ e.v., $D(C\text{–}3H) \geq 11.2$ e.v., $D(CH_3\text{–}H) \leq 4.2$ e.v., $D(CH_3\text{–}Cl) \leq 3.4$ e.v., $D(CH_3\text{–}Br) \leq 3.1$ e.v., and $D(CH_3\text{–}I) \leq 2.3$ e.v. The measured ionization potentials are $I(CH_4^+) = 13.1$ e.v., $I(CH_3Cl^+) = 11.3$ e.v., $I(CH_3Br^+) = 10.5$ e.v., and $I(CH_3I^+) = 9.6.$ e.v. The derived $I(CH_2^+)$ is ≤ 12 v.

In the mass spectrometer ions are formed by collisions of electrons with molecules and separated according to their mass to charge ratio, following the relation $m/q = r^2B^2/2V$ where r is the radius of the ion path in meters, B is the magnetic induction in webers per meter^2, V is the ion accelerating voltage in volts, m is the mass of the ion in kilograms, and q is the charge on the ion in coulombs. One can measure in the ion gun the appearance potential or the minimum energy required to produce a particular ion. The appearance potential of undissociated ions often check and supplement spectroscopic data. For many substances the data are unique. The ionization potentials of radicals and the bond energies which may be computed provide valuable knowledge toward the understanding of molecular structure.

Electron impact studies in tri and higher atomic gases are complicated by a lack of information concerning the identities of the fragments pro-