[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 798]

Some Revisions of the Covalent Radii and the Additivity Rule for the Lengths of Partially Ionic Single Covalent Bonds*

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Introduction.—In the investigation of the structures of molecules and crystals there have been developed empirical or semi-empirical systems of standard bond lengths or of atomic or ionic radii[2] which together with other structural information provide a useful basis for predictions of approximate structures of molecules and crystals. Moreover, if the significance of such a system is known, say in terms of a theory of electronic structure, then it may be used as a basis for discussing differences between observed bond lengths and those predicted by the system in terms of special features of the electronic structure. In this paper we shall discuss several suggested modifications of the Pauling and Huggins system of covalent radii[3] primarily with reference to simple gas molecules in which the chemical bonds may be regarded as single, essentially covalent[4] bonds.

The tables of covalent radii of Pauling and Huggins[3] were empirically formulated for bonds which are largely covalent; the expected length of such a bond is given by the sum $r_A + r_B$ of the appropriate covalent radii. For example, in the ethane, chlorine, and carbon tetrachloride molecules, where carbon and chlorine exhibit their normal valence in forming essentially covalent single bonds, the bond lengths are given by the appropriate sums; in ångström units $r_{C-C} = 1.54 = 0.77 + 0.77$, $r_{Cl-Cl} = 1.98 = 0.99 + 0.99$, and $r_{C-Cl} = 1.76 = 0.77 + 0.99$. If the valence configuration is not the normal one, other sets of covalent radii are employed, as for double and triple bonds, or the tetrahedral, the octahedral, and the square configurations which frequently occur in crystals.

Recent interatomic distance measurements on fluorine, hydrogen peroxide, and hydrazine seem to require an upward revision of the covalent single bond radius values of fluorine, oxygen and nitrogen. When these revised values are used many bond lengths which obeyed the additivity rule with the old values now appear to be significantly less than the sum $r_A + r_B$, while the bond lengths for electronegative pairs (F–O, Cl–O, etc.) are likewise generally less than or equal to the radius sums although they are greater than the lengths derived from the old radii. We find that for presumptive single bonds these and other deviations from additivity are represented fairly satisfactorily by the third term of the equation[5]

$$r_{AB} = r_A + r_B - \beta|x_A - x_B| \qquad (1)$$

which relates the bond length r_{AB} to the normal single covalent bond radii r_A and r_B, a constant $\beta = 0.09$, and the absolute value of the difference of the Pauling electronegativities[4] x_A and x_B of the bonded atoms. It is reasonable to infer that the deviation from additivity represented by $-\beta|x_A - x_B|$ is associated with the extra ionic character of the bond A–B as compared to the ionic character of a normal covalent bond between like atoms. We believe that this result provides the answer to the much discussed[6] question of the existence of an important effect of ionic character on the length of an essentially covalent bond. The covalent radii and the additivity rule are not strictly applicable to the (polar)

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* Presented at the Fifth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, Columbia University, New York, December 30, 1940 to January 1, 1941.

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(2) For notes on the history of systems of bond radii see L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, 2nd edition, pp. 164, 349 (154, 329 in ed. 1).

(3) L. Pauling and M. L. Huggins, *Z. Krist.*, (A) **87**, 205 (1934), reference 2, Chapter 5.

(4) Reference 2, Chapter 2.

(5) Equation 1 does not have the form which is characteristic of most of the equations representing the properties of matter in that the derivatives of r_{AB} with respect to $x_A - x_B$ are not continuous, and in fact do not exist for $x_A - x_B = 0$, but we believe that this is of no importance. Equation 1 should be regarded from the practical point of view as a simple representation which is as accurate as is justified by the data. It is of course not to be expected that any equation involving only atomic properties should give an exact representation of bond lengths.

We find that the agreement with Equation 1 cannot be appreciably improved by using electronegativity values different from those derived from bond energies by Pauling. It may therefore be noted that according to Equation 1 and Pauling's relation[4] between bond energies and electronegativity differences the deviation from additivity of bond lengths is related to the deviation from additivity of bond energies by a simple proportionality $(\Delta r_{AB})^2 \propto \Delta D_{A-B}$. It must be emphasized that this result does not imply a general relation between bond energy and bond length inasmuch as the covalent radii and the normal covalent bond energies do not appear to be simply related.

(6) See L. Pauling, Ref. 2, page 163; L. O. Brockway and H. O. Jenkins, THIS JOURNAL, **58**, 2036 (1936); Gregg, Hampson, Jenkins, Jones and Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

bonds, having extra ionic character, formed between atoms of different electronegativity.

The body of this paper is devoted to further discussion, a more detailed consideration of the covalent radii, and a rather extensive but quite incomplete comparison of observed bond distances with the values given by the additivity rule and by Equation 1.

Normal Covalent Single Bond Radii.—It is well known that the length of an essentially covalent bond depends upon its multiplicity (the double bond A=A is shorter than the single bond A–A), and it seems reasonable that it should in some way depend also on the ionic character, as is suggested by Equation 1. A natural system of covalent single bond radii for use with normal valence configurations should accordingly be derived from the lengths of homopolar single bonds in which the atoms involved exert their normal valence. In such bonds the ionic character, that is, the total contribution of ionic structures to the wave function representing the bond, is only that small amount which is characteristic of the normal covalent bond as defined by Pauling.[4]

We accordingly suggest for the single covalent radii of nitrogen, oxygen, and fluorine the respective values 0.74, 0.74 and 0.72 Å. taken from the corresponding interatomic distances 1.47, 1.48 and 1.44 Å. found in recent electron diffraction experiments on hydrazine,[7] hydrogen peroxide,[7] and fluorine.[8] The values for nitrogen (0.70 Å.) and oxygen (0.66 Å.) given by Pauling and Huggins were taken from a curve drawn through the point for carbon (0.77 Å.) and the point for fluorine (0.64 Å.) which was taken from the interatomic distance in the lower state involved in the Gale and Monk bands.[9] It is now known that this state is not the ground state of the fluorine molecule, and accordingly the only significance of these values for N, O, and F is that, in general, they lead to the correct lengths for bonds, with carbon and other atoms of similar electronegativity, having an average amount of ionic character. The exact agreement between the Pauling–Huggins normal and tetrahedral radii for oxygen is probably fortuitous inasmuch as it now seems likely that the Zn–O distance in the zinc oxide crystal, from which the tetrahedral radius of oxygen was derived, is less than the normal covalent (additivity) value because of the ionic character of the Zn–O bond, but not to the extent that would be expected from Equation 1 because of the greater coördination number of the oxygen atom.

In Table I we give for a number of atoms the Pauling–Huggins normal covalent single bond radii,[3] our new or revised values, and the electronegativities on the Pauling scale.[4] With Equation 1 we use as the radius of the hydrogen atom one-half of the interatomic distance in H_2 rather than the specially adjusted value[10,3] required to obtain agreement with observed hydride distances using the additivity rule. We believe that the radii for which we give no revised values are still the best values available. They were obtained from elementary molecules or crystals in which the atoms display their normal valence; the carbon radius from diamond, the chlorine radius from the chlorine molecule, and so on. There is the possible objection, however, that the values for the elements of the second and lower rows of the periodic table may actually be characteristic of bonds having a certain amount of

TABLE I[a]

H				
0.37				
0.30				
2.1				
Li	C	N	O	F
1.34	..	0.74	0.74	0.72
..	0.77	0.70	0.66	0.64
1.0	2.5	3.0	3.5	4.0
Na	Si	P	S	Cl
1.54	..	..	..	..
..	1.17	1.10	1.04	0.99
0.9	1.8	2.1	2.5	3.0
K	Ge	As	Se	Br
1.96	..	..	..	..
..	1.22	1.21	1.17	1.14
0.8	1.7	2.0	2.4	2.8
Rb	Sn	Sb	Te	I
2.11	..	..	..	..
..	1.40	1.41	1.37	1.33
0.8	1.7	1.8	2.1	2.4
Cs				
2.25				
..				
0.7				

[a] In the first row below each chemical symbol is given the new or revised covalent radius value if it is different from the Pauling–Huggins value given in the second row. The electronegativities x_A are given in the third row.

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(7) Preliminary values, P. A. Giguère and V. Schomaker.

(8) L. O. Brockway, THIS JOURNAL, **60**, 1348 (1938); M. T. Rogers, V. Schomaker and D. P. Stevenson, *ibid.*, **63**, (1941).

(9) *Astrophys. J.*, **69**, 77 (1929).

(10) D. P. Stevenson, *J. Chem. Phys.*, **8**, 285 (1940).

double bond character. This possibility must certainly be looked into if it is desired to explain or interpret the anomalies encountered in the application of our equation, but it seems best not to consider it further at this time.

The new radii for lithium, sodium, and potassium were obtained from the band spectral values[11] of the interatomic distances in Li_2, Na_2, and K_2, while estimates of the values for cesium and rubidium and of the interatomic distances in the other alkali molecules were got from the reported vibrational frequencies[11] and a Badger's-rule[12] line fitted to the points for Li_2, Na_2, and K_2. These derived values are certainly very rough—the value for LiCs (Table II) is obviously bad. As will be seen in Table II the sodium bond lengths (with the exception of the interalkali values) are uniformly greater than those given by Equation 1 suggesting either an increase of about 0.1 Å. in the sodium radius or a special and unreasonable value for the sodium electronegativity. The anomalous situation of sodium is also shown by comparison of the ratios of the metallic radii with the covalent radii given in Table I, and with the covalent radius values which would give exact agreement with Equation 1 for the hydrides. For Li, Na, K, Rb, and Cs these ratios have the values 1.13, 1.14; 1.21, 1.14; 1.18, 1.16; 1.16, 1.15; 1.16, and 1.16, respectively.

Comparison of the Additivity Rule and Equation 1 with Observed Bond Lengths.—In Tables II and III observed bond lengths are compared with the additivity rule sums for the revised normal single covalent radii and for the Pauling–Huggins radii, and the values computed from Equation 1 with $\beta = 0.09$. In Table III the specific references to compounds are omitted in the concluding section on unmixed halides (where there can be no confusion) and in certain other cases when there is especially good agreement among the values found in various compounds. The selection of data is not intended to be complete; instead, its purpose is to give a fair idea of how well the new system works as compared to the old one. The most important features of the comparisons are the following. For the diatomic molecules, and the molecules involving only the first row elements, Equation 1 agrees satisfactorily with the observed values over an essentially continuous range of bond types extending from the normal-covalent to the essentially ionic, whereas the additivity rule becomes sensibly incorrect for even relatively small electronegativity differences when the revised values of the covalent radii are used, and often fails badly even when the old radius values are used. For about half of the halides listed, those in which the distances tend to be anomalously short according to both systems, the agreement with our equation is much better than with the additivity rule, but for the heavier halides and for many of the carbon bonds the additivity rule is fairly or quite satisfactory[6] whereas our equation gives too large values. Equation 1 and

TABLE II

DIATOMIC MOLECULES

Bond	$r_{\text{obsd.}}$	$r_A + r_B$	$r_{\text{calcd.}}$[a]	Σr_{P-H}[f]
Alkalies				
LiK	3.30[b]	3.30	3.28	
LiRb	3.50	3.45	3.43	
LiCs	3.75	3.59	3.56	
NaK	3.50	3.50	3.49	
NaRb	3.59	3.65	3.64	
NaCs	3.76	3.79	3.77	
RbCs	4.36	4.36	4.35	
Alkali hydrides				
LiH	1.60[c]	1.71	1.61	
NaH	1.89	1.91	1.81	
KH	2.24	2.33	2.22	
RbH	2.37	2.48	2.36	
CsH	2.49	2.62	2.49	
Hydrogen halides				
HF	0.92[c]	1.09	0.92	0.94
HCl	1.28	1.36	1.28	1.29
HBr	1.41	1.51	1.45	1.44
HI	1.60	1.70	1.67	1.63
Alkali halides				
NaCl	2.51[d]	2.53	2.34	
NaBr	2.64	2.68	2.34	
NaI	2.90, 2.83[e]	2.87	2.73	
KCl	2.79	2.95	2.75	
KBr	2.94, 2.96	3.10	2.90	
KI	3.23, 3.13	3.29	3.15	
RbCl	2.89, 2.95	3.10	2.90	
RbBr	3.06	3.25	3.07	
RbI	3.26, 3.36	3.44	3.30	
CsCl	3.06, 3.07	3.24	3.03	
CsBr	3.14, 3.18	3.39	3.20	
CsI	3.41, 3.43	3.58	3.43	

[a] $r_{\text{calcd.}} = r_A + r_B - 0.09\,|x_A - x_B|$. [b] See text. [c] From reference 11. [d] Electron diffraction values, reference 15. [e] Estimated by a semi-empirical procedure from the interatomic distance in the crystal, May, *Phys. Rev.*, **54**, 629 (1938). [f] The sum of the Pauling–Huggins covalent radii.

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(11) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," Prentice-Hall, Inc., New York, N. Y., pp. 482 ff.

(12) R. M. Badger, *Phys. Rev.*, **48**, 284 (1935).

the natural hydrogen radius $r_H = 0.37$ lead to satisfactory results for the lighter hydrides, but for the others the agreement appears to be not so good as that obtained with the additivity rule and the value $r_H = 0.30$.

TABLE III

POLYATOMIC MOLECULES

Bond	Compound	$r_{\text{obsd.}}$	$r_A + r_B$	$r_{\text{calcd.}}$[a]	Σr_{P-H}[b]	Reference
Hydrides						
CH	CH_4	1.09	1.14	1.10	1.07	2, page 168
NH	NH_3	1.01	1.11	1.03	1.00	2, page 168
OH	H_2O	0.97	1.11	0.98	0.96	2, page 168
SiH	SiH_4	1.42	1.54	1.51	1.47	13
		1.46				10, from Badger's rule
PH	PH_3	1.40	1.47	1.47	1.40	10, from Badger's rule
		1.46				14
SH	H_2S	1.35	1.41	1.37	1.34	2, page 168
AsH	AsH_3	1.54	1.58	1.57	1.51	10, from Badger's rule
		1.56				14
SeH	H_2Se	1.50	1.54	1.51	1.47	10, from Badger's rule
Carbon bonds						
NC	$N(CH_3)_3$	1.47	1.51	1.46	1.47	15
OC	$(CH_3)_2O$	1.42	1.51	1.42	1.43	15
FC	CH_3F	1.39	1.49	1.35	1.41	15, 16
	CF_4	1.36				15
SiC	SiC	1.89	1.94	1.88		3a
	$Si(CH_3)_4$	1.93				15
PC	$P(CH_3)_3$	1.87	1.87	1.83		15
SC	$S(CH_3)_2$	1.82	1.81	1.81		15
ClC		1.76	1.76	1.71		15, 17
GeC	$Ge(CH_3)_4$	1.98	1.99	1.92		15
AsC	$As(CH_3)_3$	1.98	1.98	1.93		15
BrC		1.91	1.91	1.88		15
SnC	$Sn(CH_3)_4$	2.18	2.17	2.10		15
IC	CI_4, CHI_3	2.12	2.10	2.09		15
Nitrogen bonds						
NN	N_2H_4	1.47	(1.48)	(1.48)	1.40	6
NO	CH_3ONH_2	~1.43	1.48	1.43	1.36	18
NCl	$(CH_3)_2NCl$	1.77	1.73	1.73	1.69	
	$(CH_3)NCl_2$	1.74				
	NOCl	1.98				15
NBr	NOBr	2.14	1.88	1.86	1.84	15
Oxygen bonds						
OO	H_2O_2	1.48	(1.48)	(1.48)	1.32	6
OF	F_2O, FNO_3	1.41	1.46	1.41	1.30	15
OCl	Cl_2O	1.68	1.73	1.68	1.65	15
Halogens						
FF	F_2	1.44	(1.44)	(1.44)	1.28	7
ClF	ClF	1.64	1.71	1.62	1.63	19
ICl	ICl	2.32	2.32	2.27		15
Other normal valence non-metallic halides YX_n						
SiF		1.54	1.89	1.69	1.81	15
PF		1.52	1.82	1.65	1.74	15
AsF		1.72	1.93	1.75	1.85	15
SiCl		2.02	2.16	2.05		15
PCl		2.09	2.09	2.01		15
SCl		1.99	2.03	1.98		15
GeCl		2.08	2.21	2.09		15
AsCl		2.16	2.20	2.11		15
SiBr		2.14	2.31	2.22		20
		2.19				15
PBr		2.23	2.24	2.18		15
GeBr		2.32	2.36	2.26		15
AsBr		2.34	2.35	2.28		15
GeI		2.48	2.55	2.49		15
PI		2.47	2.43	2.40		15
AsI		2.54	2.54	2.50		15

[a] $r_{\text{calcd.}} = r_A + r_B - 0.09|x_A - x_B|$. [b] The sum of the Pauling–Huggins covalent radii.

We believe that the successes of Equation 1 are nevertheless sufficiently general and clear-cut to make it a promising beginning for a satisfactory system for discussing or predicting bond lengths, and to show that the lengths of bonds are significantly affected by even quite small amounts of ionic character.

We are indebted to Professor Pauling for much helpful discussion and criticism.

Summary

New values of the normal covalent single bond radii of hydrogen, nitrogen, oxygen and fluorine are given which are consistent with the bond lengths in the hydrogen, hydrazine, hydrogen peroxide, and fluorine molecules. The additivity rule for bond lengths is not generally valid, but must be used with a correction for the effect of the ionic character of the bond.

PASADENA, CALIF. RECEIVED OCTOBER 17, 1940

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(13) W. B. Steward and H. H. Nielson, *Phys. Rev.*, **47**, 828 (1935).

(14) Sutherland, Lee and Wu, *Trans. Faraday Soc.*, **35** 1373 (1939).

(15) L. R. Maxwell, *J. Optical Soc. Am.*, **30**, 375 (1940).

(16) D. M. Dennison, *Rev. Modern Phys.*, **12**, 175 (1940); unpublished electron diffraction reinvestigation by D. P. Stevenson and V. Schomaker.

(17) We have reinvestigated methyl chloride by electron diffraction and find $r_{C-Cl} = 1.77$ Å., the result previously obtained by this method.

(18) Reinvestigation by electron diffraction, D. P. Stevenson and V. Schomaker. The earlier value (15) is 1.37.

(19) Preliminary electron diffraction value, A. Wahrhaftig.

(20) From unpublished electron diffraction measurements on $SiBr_4$, $SiHBr_3$, SiF_2Br_2, W. J. Howell, R. Spitzer and V. Schomaker.