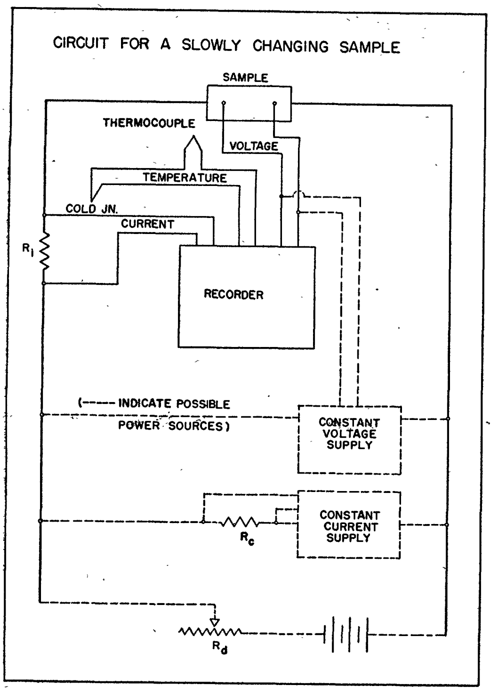

FIG. 5. A circuit for slowly changing samples.

relay in order to keep the voltage on scale. The standard resistances across which the current is read can also be varied by means of a relay to provide for automatic scale changing. Pole 6 of the relay selects a voltage from a scale circuit, which is then printed on the record.

A voltage is applied to the point preceding the series of readings and thus prevents spurious tripping of the relays.

The circuit selector switch is used to select the input to the Vibrating Reed Electrometer and to select the points on which the relays will be actuated. The output of the electrometer, as well as all other voltages, is then applied to the recorder through the recorder input switch.

The simplest use with a non-ohmic sample is the resistance measurement of a rectifier. Fig. 3 shows a schematic circuit of this type. Again, for simplicity, only 5 points are shown on the switches. The current scale, scale indicator, temperature voltage, and current measurement are the same as shown in Fig. 2. By means of relay R_2, the sample is reversed each cycle of the recorder. The voltage-controlled power supply can provide a different voltage for each point. By monitoring the voltage and reading scale indicator for every other current point, and recording temperature once each cycle, 6 points of the rectifier curve can be followed for both directions of the rectifier, giving a complete characteristic curve about once every 2 min.

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An Interpretation of Bond Lengths and a Classification of Bonds

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A visualizable representation of atoms in combination which would help to explain observed bond lengths has long been needed. An empirical method of correcting covalent radius sums for electronegativity differences has been proposed (*1*), but objections have been raised (*2*). "Anomalous" lengths of both single and multiple bonds are customarily ascribed to "resonance" among covalent and ionic, or single and multiple bond structures (*3–5*), an explanation which is far from satisfying (*6*) and is artificial in many of its applications, without being completely helpful in permitting a clear concept of the nature of the molecular structures. A method which allows ready visualization and which has been quite successful, not only for estimating bond lengths but also in classifying bond types according to length, is here outlined.

The physical picture permitted by this method is simple and straightforward. It is well known that the electronic spheres of atoms expand when electrons are taken on to form negative ions, and contract when electrons are removed to form positive ions. It seems perfectly reasonable to suppose that such change in size is not restricted to ion formation but occurs much more generally, whenever the electrons involved in a covalent bond spend more than half-time more closely associated with one atom than with the other. This would be in any polar covalent bond.

The time-average equilibrium position of two electrons forming a covalent bond must be such that the attraction of both atoms for the electrons is equal. If the attraction was initially unequal, this means that an adjustment has occurred. In the equilibrium position, the valence electrons must be more closely associated with the atom which initially attracted them more. In effect, this atom has assumed a fractional negative charge. This causes its electronic sphere to expand, so that its radius increases. As its radius increases, its attraction for the valence electrons decreases. The other atom similarly has assumed a fractional positive charge, causing a contraction of its electronic sphere, decreasing the radius. As its radius decreases, the attraction of this atom for the valence electrons increases. This adjustment of the radii of the atoms ceases when their attraction for the electrons has become equal. The bond length is the sum of the *adjusted radii.*

In a covalent bond, the attraction of an atom for the valence electrons is the electronegativity (3). Therefore, if a quantitative relationship between electronegativity and atomic radius were known, it could serve as a basis for calculating the adjusted radii and therefore the bond lengths, assuming the electronegativities to become equal in the process of bond formation.

A function of the atomic radius which appears to be also a measure of electronegativity has been found. This function, called the "stability ratio (SR)," has been used successfully in the calculation of practically all gas phase bond lengths reported in the literature (*7*) except for bonds with hydrogen. For 95% of these bonds, the mean deviation of calculated from reported lengths was less than 0.03A. The derivation of the stability ratio is as follows:

The average number of electrons/cu A of an atom or ion may be calculated using the expression $ED = 3Z/4\pi r^3$, where ED is the average electronic density, Z is the number of electrons, and r is the nonpolar covalent radius or the ionic radius. The ED's of the inert elements, calculated from radii suggested by Pauling (*8*), are: He 0.61, Ne 1.70, A 1.18, Kr 1.78, Xe 1.87, Rn 1.93. It has been observed that these values are different from those of all active elements and their ions. Assuming that the ED's of the inert atoms represent maximum chemical inactivity corresponding to their particular atomic numbers, the chemical reactivity, or in a sense the electronegativity, of atoms and ions of the active elements may be represented by the ratio of their ED to the ED of an inert atom (real or determined by linear interpolation between real values) having the same number of electrons. This ratio is called the stability ratio. SR's for most of the elements and their common ions have been determined.

It is postulated that when atoms differing in SR combine, they change in size until they are equal in SR in the molecule, which is equivalent to saying that their attractions for the valence electrons, or electronegativities, become equal. The SR of the molecule is the geometric mean of the individual SR's of the atoms before combination. This permits the calculation of atomic radii effective within the molecule, by

$$r = \sqrt[3]{\frac{Z}{4.19\, ED_i\, SR_m}}, \qquad (1)$$

where Z is the electronic number, ED_i represents maximum stability, and SR_m is the SR in the molecule. The bond length is then determined as the sum of two radii. The "shortening" due to electronegativity differences (*1*) is readily explained, as the contraction of the less electronegative atom usually exceeds the expansion of the other. This is especially true when, as commonly happens, there are several more electronegative atoms surrounding a central less electronegative atom.

This method is sufficient for the calculation of approximately half of the nearly 700 bonds investigated. Its application to the alkali halide gas molecules is reported elsewhere (*9*). The rest of these bonds, which include some "single" and all multiple bonds, are shorter than appears to be accounted for by this correction for electronegativity differences. The necessary supplementary correction is based on geometric concepts related to the theory of directed valence. The simplified picture for the bonds whose lengths are calculated satisfactorily by use of Equation (1) is of electrical spheres in tangential contact. Closer than tangential contact is considered to be possible, without any change in the average electronic density, if the spheres become deformed in their region of contact.

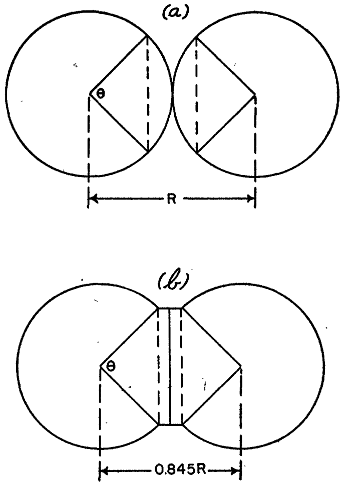

FIG. 1. Deformation in double bonding.

A simple way of picturing this deformation is to imagine the deformed portion of each sphere to consist, before deformation, of a spherical segment with the line connecting the two nuclei passing perpendicularly through the center of its base. As the spheres approach closer from the point of tangential contact, each spherical segment becomes flattened, assuming finally the shape of a cylindrical section having the same base and the same volume as the original segment. The nearness of approach will then be a function of the diameter of the base. One may picture the diameter of the base as being limited or defined by lines representing atomic orbitals, or by lines midway between such orbitals, drawn at orthogonal or tetrahedral angles as radii of the sphere. Two such atomic spheres (*a*) in tangential contact, and (*b*) in closer contact as limited by two orthogonal orbitals, are depicted in Fig. 1. This representation must of course

TABLE 1

Bond length factors

Type	Description of atomic contact	n	F
Ia	Tangential	0	1.000
II	Half double:		
a	Orthogonal	2	0.923
b	Tetrahedral	3	.885
III	Double:		
a	Orthogonal	4	.845
c	Mixed	5	.808
b	Tetrahedral	6	.770
IV	Triple:		
a	Orthogonal	6	.770
d	Mixed	7	.730
c	Mixed	8	.691
b	Tetrahedral	10	0.611

TABLE 2

Partial Summary: Classification of Bonds According to Lengths

Type	Description	No. examples	Mean deviation from observed	Exceptions noted
Ia	All electron-sufficient single bonds except as noted below, and including gaseous alkali halides	310	0.033	34 bonds deviation ≧ 0.10A from observed
IIa	1) Bonds to triple bond C	14	.023	None
	2) Single between 2 double bonds	2	.010	"
	3) Cl, Br, I to unsaturated C	25	.025	"
	4) Cl, Br, I to Zn, Cd, Hg	8	.026	"
	5) Most single bonds to N, O, F* except with very electronegative atoms	83	.025	
	6) P—O bonds in oxyhalides	8	.016	$POBr_3$ (IIIc)
	7) S_2, Se_2, Te_2	3	.042	None
IIb	1) Double bonds between completely or almost completely halogenated C atoms	8	.022	"
	2) Single between 2 triple bonds	3	.007	"
	3) C—C bonds in aromatic rings	15	.025	"
	4) C—S double bonds	2	.015	"
IIIa	1) Aliphatic double bonds	11	.019	IIb, (1)
	2) S—O and Se—O in oxides and oxyhalides	8	.010	None
	3) O_2 and O_3	2	.025	"
IIIb (or IVa)	1) All C—C and C—N triple bonds	14	.019	"
	2) Multiple, type —N=O	6	.025	"
	3) C—O multiple, including C oxides, organic and inorganic carbonyl	32	.023	BH_3CO (IVc) CO, acetone (IVd)
IIIc	1) Multiple, type ≡N=O	8	.021	$FONO_2$ (IIb)
	2) S—O in sulfoxide, sulfone	2	.015	None
IVd	1) CO and N_2	2	0.015	"

* Perhaps explicable as resulting from involvement of other orbitals in bonding, made possible in first row atoms when closer approach results from large electronegativity differences.

become less adequate when the atoms are different in size.

The effective radius of an atom in the direction of its bond may then be determined as the product of the radius as estimated by Equation (1), and a factor F dependent on the angle θ. The factors for two and for three orbitals, orthogonal and tetrahedral, have been calculated by methods of trigonometry and geometry, and are listed in Table 1. Also listed are symmetrically spaced intermediate factors, which have been found necessary for a systematic representation of the relation of bond types to bond lengths. For example, the factor 0.923 used for most single bonds to N, O, or F is midway between 1.000 and 0.845, which is calculated for contact between two atoms, each using two orthogonal orbitals for the bond, and is applicable to all olefinic double bonds. It is observed that these factors are all related, being represented by $F = 1 - na$, where n is an integer and a is a constant equal to 0.0385. Values of n are also listed in Table 1. It will be observed that n corresponds to the number of electrons usually considered to participate in the bonding, for ordinary double and triple bonds.

Practically all the more than 300 bond lengths not adequately accounted for by use of Equation (1) alone may be satisfactorily determined by multiplying the Equation (1) length by the proper value of F. This method might seem of doubtful significance because the F values are so close together, if it were not for the fact that the relationships between bond type and bond factors are entirely too consistent to be coincidental.

The major results of this study of bond lengths are very briefly summarized in Table 2.

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