Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Velocity of Sound as a Bond Property

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RECENTLY in this Journal Rao[1] has pointed out that the function $V=v_s^{1/3}M/d$, where v_s is the velocity of sound, is a constant characteristic of a pure liquid, and is additive and constitutive in that it may be computed by summing increments assigned to atoms and bonds.

An alternative procedure for computing this constant is to assume that there is an additivity only of what we choose to call "bond velocities." Thus for the paraffins we have $(n-1)(C-C)+(2n+2)(C-H)=V$, where the constant V, which varies from liquid to liquid, may be regarded as analogous to the molecular refractivity and termed the "molecular sound velocity." On this assumption equations have been set up for the members of several homologous series using the experimental values of V listed by Rao, and solved for the bond increments. The method of least squares was employed on the paraffins to find the C—C and C—H increments which were then used to secure other bond velocities from other series. This has resulted in the tentative average values given in Table I.

TABLE I. Bond velocities.

Bond	Bond increment	Bond	Bond increment
C−H	95.2	C−Cl	230
C−C	4.25	C=C	129
C−O	34.5	C=O	186
O−H	99.0		

TABLE II. Experimental and calculated molecular sound velocities.

	Molecular sound velocity		
Liquid	Experimental	Calculated from bond increments	Calculated from Rao's increments
Pentane	1160	1159	1160
Hexane	1356	1354	1355
Heptane	1545	1549	1550
Octane	1746	1743	1745
Methyl acetate	851	830	843
Ethyl acetate	1037	1025	1038
Propyl acetate	1211	1220	1233
Butyl acetate	1408	1414	1428
Amyl acetate	1598	1609	1623
Methyl alcohol	421	419	454
Ethyl alcohol	624	614	649
Propyl alcohol	806	809	844
Butyl alcohol	1004	1003	1039
Amyl alcohol	1198	1198	1234
Benzene	979	971	945
Toluene	1170	1166	1140
Xylene	1362	1360	1335
Cymene	1731	1750	1725
Acetone	781	766	769
Diethylketone	1161	1155	1159
Methylhexylketone	1720	1739	1744
Methylene chloride	649	650	649
Ethylene chloride	846	845	844

In Table II are listed the experimental values of V, those computed using the atomic and bond values given by Rao, and those computed with the bond values of Table I. The present assumption yields as good agreement with experiment as does Rao's assumption, and is, moreover, more simple. It neglects, of course, single-double bond resonance and any variations in bond values in different molecules or different series.

Certain relations of the bond velocities to other bond properties have been found. These will be discussed at another time.

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[1] M. Rama Rao, J. Chem. Phys. 9, 682 (1941).

Quantization of Molecules

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THE difference in the internuclear distance* of H_2 (0.74A) and Li_2 (2.67A) can be understood by assuming a different quantization of the electron pair binding the $2H^+$ and $2Li^+$, respectively. The comparison with the ideal unpolar Bohr model led[1] to the assignment $n=1$ for H_2 and $n=2$ for Li_2 for the principal quantum number of these electrons.

The idea of W. Kossel and G. N. Lewis of complete noble gas shells and the concept of interaction between atomic cores[2] and electrons prove to be useful for the quantization of other covalent molecules.

The H_2 molecule is a diatomic analog of the He atom, inasmuch as both particles have $n=1$ and have weak external fields. The difference between them is due to the splitting of the He^{++} into $2H^+$.

Elements of atomic numbers 2 to 6 do not form gaseous diatomic molecules at N.T.P. The analogy between physical properties of N_2 (and CO) and argon has been emphasized by Langmuir.[3] He proposed a model consisting of two N^{5+} cores, and two electrons near them, surrounded by a (cubical) noble gas configuration of 8 electrons. As has been shown[4] on the basis of crystal structure, molar volume, and refraction, the isoelectronic particles $C_2^{=}$; NC^-; N_2; CO; NO^+; (O_2^{++}?) have outer shells which deviate only slightly from the spherical symmetry of the noble gases.

Since N_2 has 10 electrons beyond its two K groups, one can compare N_2 with Ne by splitting the charge of Ne^{10+} into $2N^{5+}$. In accord with the general principle[5] that the splitting of a nucleus within a given electronic shell leads to a loosening of the latter, one finds: the molar refractions of He and H_2 are 0.5 cc and 2.0 cc; those of Ne and N_2 are 1.0 cc and 4.0 cc, respectively.

This loosening of the electronic system is accompanied by a strengthening of the external field of the molecule; with respect to the boiling point, H_2 is nearer to Ne than to He, and N_2 is nearer to Kr than to Ne.

The significance of the ten electron shell is also shown in a maximum of binding strength (maximum in force constant, minimum in distance), e.g., in the series C_2, N_2, O_2, F_2; BeO, BO, CO, NO, O_2; C_2, C_2H_2, C_2H_4, C_2H_6.

The above facts and the quantum formula of the neon atom $1s^22s^22p^6$, lead one to sharpen Langmuir's picture of N_2 by allocating the principal quantum number $n=1$ to a group of 2 electrons and $n=2$ to a group of eight electrons. It has been emphasized[1] that the principal quantum number of the electrons nearest to the bonded cores can be expected to depend on the spacial extension of the electronic system of the latter. The fact that N^{5+} is much smaller than Li^+ and the internuclear distance in N_2 ($r=1.09$A) is also smaller than in Li_2 ($r=2.67$A, $n=2$) gives additional support to the quantum formula of N_2 : KK; 1^22^8. A subdivision of the eight electron shell has to be based on spectroscopic considerations.[2b]

While each of the two pairs of K electrons of N_2 is quantized with respect to one of the two nuclei N^{7+}, the third pair with $n=1$ and the 8 electrons with $n=2$ are quantized with respect to the field of both N^{5+}. Therefore the above does not contradict the Pauli principle which in its original form applies to monatomic particles.

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[*] The data on diatomic molecules used in this and the following two letters are from G. Herzberg (see reference 2b). Some of the other data are from L. Pauling, *The Nature Of The Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition.

[1] T. Berlin and K. Fajans, J. Chem. Phys. **10**, 691 (1942).

[2] a. The methods of applying quantum theory to molecules developed by Heitler, London, Pauling, and Slater as well as that of Hund, Lennard-Jones, and Mulliken compare the molecules with atoms. b. See G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).

[3] I. Langmuir, J. Am. Chem. Soc. **41**, 901 (1919). See also W. Kossel, Ann. d. Physik **49**, 360 (1916).

[4] K. Fajans and T. Berlin, Buffalo Meeting of the American Chemical Society, September, 1942. The detailed papers will be published soon.

[5] E.g., the molar refraction increases in the series Ne, HF, H_2O, H_3N, H_4C from 1.0 to 6.5 cc. (See N. Bauer and K. Fajans, J. Am. Chem. Soc. December, 1942.) The refraction of C_2H_4 is 10.3 that of B_2H_6 is 12.9 cc.

Difficulties in the Valence Bond Theory*

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THE subdivision of the 10 valence electrons of N_2 into the groups of 2 and 8 electrons (see III) is not in accord with its usual electronic formula : N : : : N : indicating a triple bond.

It can be shown that this contradiction adds to the difficulties of Kekulé's valence bond theory and its usual electronic interpretation.

In N_2^+ the force constant is smaller, the internuclear distance (1.117A) is larger than in N_2. Therefore, the detached tenth electron strengthened the binding of the two N^{5+} cores. One has to conclude that the other 9 electrons are also bonding since the ionization process eliminates the electron which is most loosely bound and there is (see III, footnote 4) a close interrelation between the strength with which the electrons are bound and that with which they bind the cores. Thus, all ten and not merely six electrons take part in the binding of the cores.[1,2]

The usual valence bond formula of N_2 fits into the series F−F, O=O, N≡N which one is inclined to extrapolate to C≣C. The increase in dissociation energy into atoms from F_2 (65 kcal.) to N_2 (170 kcal.) could be considered as a further support of these formulae, since the energy of the carbon-carbon bond increases in the series single, double, triple bond.[3] From this point of view one would expect that the bond C≣C is still stronger than N≡N or −C≡C−. Contrary to that, the dissociation energy of C_2 into atoms is 83 kcal., i.e., of the order of magnitude of the single bond only. Moreover, C_2 has a very strong external field and thus has no noble gas character. One has also to recall that the electronic formula $:\ddot{O}::\ddot{O}:$ has already been disproved by the paramagnetism of O_2 and that other formulae have been proposed for it, e.g., $:\underset{\cdot}{\ddot{O}}:\underset{\cdot}{\ddot{O}}:$ by G. N. Lewis.[4]

Thus among the valence bond formulae of the mentioned four diatomic molecules, $:\underset{\cdot\cdot}{\ddot{F}}:\underset{\cdot\cdot}{\ddot{F}}:$ is the only one which is not in disagreement with the behavior of these elementary substances.

The usual electronic formula of N_2 and many others based on the idea of completion of a noble gas shell by sharing electrons also encounter the following difficulty. Only a limited number of atoms or radicals can assume a noble gas configuration by an exothermic process: H, F, Cl, Br, I, OH, CN, and perhaps some of the polyatomic radicals.

The oxygen ion $O^=$, however, is unstable in the free gaseous state and its electronic shell has to be stabilized, e.g., by H^+ in OH^- or by other cations (V). This is also true for N^{3-}, C^{4-}, or B^{5-}. Thus, in a symmetrical molecule N_2 one could assume a temporary polarity (II) connected with a completion of one N^{3-} stabilized by N^{3+} from the other atom. The above consideration contradicts, however, the assumption that in O_2, N_2, C_2 both atoms at the same time complete their octets.

The contention (see Pauling, III*) that many molecules, even the simplest, are the result of the resonance between a number of forms with different combinations of single, double, and other bond types can be considered as a strong criticism of the valence bond theory. For it means the sacrifice of the initial aim of the theory to represent one experimentally homogeneous molecular species by *one* formula.

The quantum formula of N_2, KK; 1^22^8, (see III) is free of these difficulties. It considers all ten electrons as common to both cores and resembles in this respect the method of molecular orbitals used (III, 2a) in the discussion of spectral data. There are, however, many types of substances to which neither a valence bond formula nor an