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THE NATURE OF THE CHEMICAL BOND. IV. THE ENERGY OF SINGLE BONDS AND THE RELATIVE ELECTRONEGATIVITY OF ATOMS

BY LINUS PAULING

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Recent developments in the application of the quantum mechanics to problems of molecular structure[1] have indicated that the properties of a bond between two atoms often are determined mainly by one single-electron orbital wave function for each atom, and are not strongly affected by the other atoms in the molecule; for when the wave function for a molecule containing single covalent bonds is set up with the use of single-electron orbital wave functions, it is found that each bond function tends to overlap to the maximum extent the other function involved in one bond, and to avoid overlapping all others, so that the resonance integrals other than those characteristic of the bonds are small. The empirical evidence of interatomic distances supports this view; it has been possible to formulate a set of covalent radii for use in purely covalent molecules (in which each atom forms covalent bonds to a number determined by its position in the periodic system) which accounts satisfactorily for observed distances in molecules to which a single Lewis electronic structure can be assigned.[2] It has also been found that changing the covalence of an atom, and hence the nature of the bond function, produces a change in the radius.[3]

Independence of the bonds in a molecule would require that the total energy of formation of the molecule from separate atoms be expressible as the sum of constant energy terms characteristic of the various bonds. This is found to be nearly true for molecules to which a single Lewis electronic structure can be assigned, the deviations from constancy of bond energy rarely exceeding 2 or 3%. Data on the heats of formation and heats of combustion of gaseous molecules may accordingly be used to evaluate the energies of various bonds. This procedure is adopted in the following pages. It is then shown that the energies of bonds, when discussed with the aid of the postulate of the additivity of the energies of normal covalent bonds, throw much light on their nature, in particular on the amount of ionic character possessed by them, and permit the localization of

[1] Linus Pauling, THIS JOURNAL, **53**, 1367, 3225 (1931); **54**, 988 (1932); J. C. Slater, *Phys. Rev.*, **37**, 481 (1931); **38**, 1109 (1931); F. Hund, *Z. Physik*, **73**, 1, 565 (1932).

[2] Linus Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932). Examples of molecules which resonate among several Lewis structures are given in this paper. Further discussion of the nitrous oxide molecule is given in a later note, Linus Pauling, *ibid.*, July, 1932.

[3] Linus Pauling and M. L. Huggins, *Z. Krist.*, to be published.

atoms on an "electronegativity map," with the aid of which their properties may be conveniently discussed. It is also found that bond energies provide evidence in regard to a number of questions relating to the structure of simple molecules, such as O_4, O_3, P_4, etc.

Extreme Ionic Bonds and Normal Covalent Bonds.—Before discussing the nature of actual bonds it is desirable to specify the sense in which the terms ionic and covalent will be used.

Early discussions of molecules such as the hydrogen halides treated them as consisting of ions which deformed each other to some extent. Now the wave functions corresponding to the normal and all excited states of F^-, for example, form a complete orthogonal set, so that any electronic structure of the HF molecule, even a normal covalent structure, could be accurately represented by a wave function built up from the wave functions for F^-, the contributions of excited states being considered to result from the deforming action of the proton. If, then, we are to distinguish at all between ionic bonds and bonds of other types, some arbitrary decision as to the extent to which excited ionic states are to be considered in constructing wave functions must be made. A number of phenomena formerly explained qualitatively as due to mutual polarization and deformation of ions have been quantitatively accounted for in other ways, and it has become evident that deformation of ions does not have the importance in determining the properties of molecules that it was formerly ascribed. Consequently I prefer, in an approximate treatment, to consider only states in which electrons occupy the most stable orbits in atoms or ions, and so to select for the wave function representing an extreme ionic molecule a function formed from those for normal undeformed ions.

A bond between two identical atoms, as H:H, Cl:Cl, C:C, etc., may be considered to be a normal covalent bond, involving a pair of electrons and two single-electron orbital wave functions, one for each atom. The wave function representing it may not be closely approximated by a function of the Heitler–London type, $\psi(1)\varphi(2) - \varphi(1)\psi(2)$, but may involve ionic terms $\varphi(1)\varphi(2)$ and $\psi(1)\psi(2)$, corresponding to A^+A^- and A^-A^+, these two occurring, of course, with the same coefficient. The contribution of these terms to the normal state of the hydrogen molecule has been discussed by Slater.[4] In the wave function representing the bond between unlike atoms A and B the terms corresponding to A^+B^- and A^-B^+ will occur with the same coefficient, equal to that for A:A or B:B, if the two atoms have the same degree of electronegativity. Such a function may be called a normal covalent bond wave function, and the bond a normal covalent bond. If one atom is more electronegative than the other, the wave function can be formed by adding to the normal covalent bond wave function an additional ionic term.

[4] J. C. Slater, *Phys. Rev.*, **35**, 509 (1930).

The Additivity of the Energies of Normal Covalent Bonds. The Hydrogen Halides and the Halogen Halides.—It is found that there exists a convincing body of empirical evidence in support of the postulate[5] that *the energies of normal covalent bonds are additive;* that is

$$A:B = {}^1/_2\{A:A + B:B\}$$

where the symbol A:B means the energy of the normal covalent bond between A and B, etc. The energy of a normal covalent bond between A and B would be given by the integral $\int \psi^* H \psi d\tau$, with ψ the normalized normal covalent wave function. Inasmuch as the energy integral for any wave function for a system must be equal to or greater than the energy of the lowest state of the system, the energy of the actual bond between A and B must be at least as great as that for a normal covalent bond. Hence if the postulate of additivity is correct, the difference Δ between the actual bond energy and that predicted from additivity must be zero or positive, and the greater the ionic character of the bond, the greater will be the value of Δ.

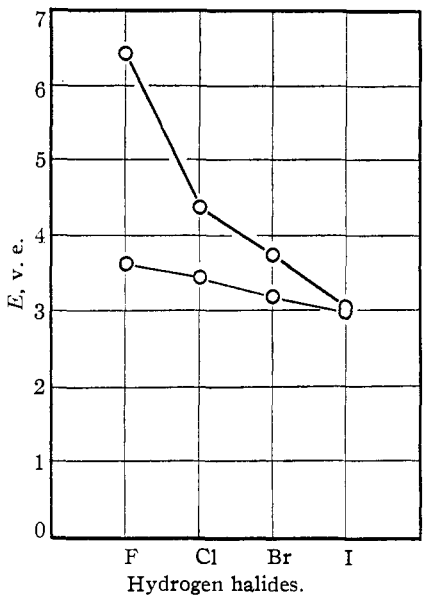


Fig. 1.—Bond energies for hydrogen halides: observed values are connected by heavy lines, values calculated for normal covalent bonds by light lines.

In Table I and Figs. 1 and 2 are given bond energies for hydrogen and the halogens, and their binary compounds, together with the deviations from additivity. The values of Δ are usually known more accurately than the bond energies themselves because they can be directly measured as heats of reaction. It is seen that *the values of Δ are positive for all of these compounds*, which provides strong support for the postulate. Moreover, the values are in agreement with previously formed conceptions as to the nature of the bonds in these molecules. A recent discussion[6] of energy curves has shown HF to be largely ionic, while HCl, HBr and HI are largely covalent, with HI nearly a normal covalent molecule. These descriptions are in complete accord with the course of the Δ-values.

BrCl approaches the normal covalent type still more closely than HI, with a deviation from additivity of less than 1%. The values of Δ for

[5] Linus Pauling and Don M. Yost, *Proc. Nat. Acad. Sci.*, **18**, 414 (1932).

[6] Pauling, THIS JOURNAL, **54**, 988 (1932).

TABLE I[5]

	H:H	F:F	Cl:Cl	Br:Br	I:I
Bond energy	4.44	2.80	2.468	1.962	1.535 v. e.
		HF	HCl	HBr	HI
Actual bond energy		6.39	4.38	3.74	3.07
Predicted from additivity		3.62	3.45	3.20	2.99
Δ		2.77	0.93	0.54	0.08
		ClF	BrCl	IBr	ICl
Actual bond energy		3.82	2.231	1.801	2.143
Predicted from additivity		2.63	2.215	1.748	2.001
Δ		1.19	0.016	0.053	0.142

IBr and ICl are also small, but that for ClF is even larger than for HCl, showing that the bond in chlorine fluoride is more ionic in character than that in hydrogen chloride.

It is perhaps desirable to point out that the bond type has no direct connection with ease of electrolytic dissociation in aqueous solution. Thus the nearly normal covalent molecule HI ionizes completely in water, whereas the largely ionic HF is only partially ionized.

Bond Energies for Light Atoms and Halogens.—In the calculation of bond energies from heats of formation and heats of combustion the following energies of reaction were assumed[7] in addition to those given in Table I.

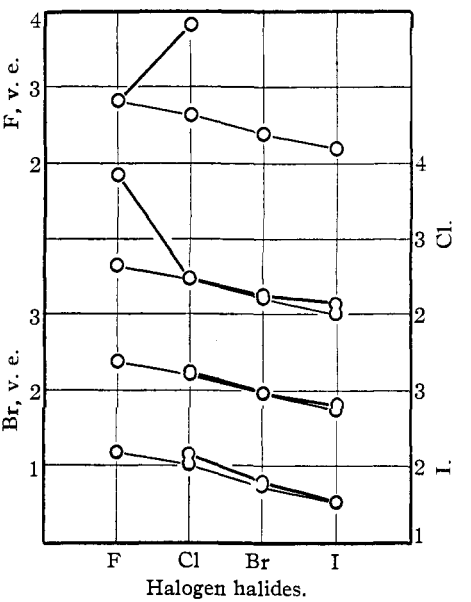


Fig. 2.—Bond energies for halogen halides.

$$2O = O_2 + 5.09 \text{ v. e.}$$
$$2N = N_2 + 9.10 \text{ v. e.}$$
$$H_2 + {}^1/_2\,O_2 = H_2O(g) + 2.508 \text{ v. e.}$$
$$H_2 + {}^1/_2\,O_2 = H_2O(l) + 2.966 \text{ v. e.}$$
$$C^3P = C_{graphite} + 6.61 \text{ v. e.}$$
$$C^{*5}S = C_{graphite} + 7.61 \text{ v. e.}$$
$$C_{graphite} + O_2 = CO_2 + 4.094 \text{ v. e.}$$
$$2Br = Br_2(l) + 2.293 \text{ v. e.}$$
$$2I = I_2(c) + 2.188 \text{ v. e.}$$

Some doubt has been thrown on the value 9.1 v. e. for the dissociation energy of N_2 by the recent experiments of Tate and Lozier,[8] whose interpre-

[7] Values of thermal quantities used throughout this paper are from "International Critical Tables," Landolt-Börnstein, or Kharasch's compilation of heats of combustion, *Bur. Standards J. Research*, **2**, 359 (1929), except where otherwise indicated.

[8] J. T. Tate and W. W. Lozier, *Phys. Rev.*, **39**, 254 (1932).

tation of their results has in turn, however, been criticized by Arnot.[9] The value 6.61 v. e. for the heat of sublimation of graphite to normal carbon atoms is very uncertain, and the assumed value of 1.00 v. e. for the excitation energy to the $2s2p^3\ {}^5S$ state is also uncertain. It is not essential for the discussion of deviations from additivity that these energy quantities be known; but it is convenient to deal with definite values for bond energies, even though they are relative to an arbitrarily chosen starting point, so that the values given have been used in this paper. When accurate values of these quantities become known, the bond energies can be easily corrected accordingly.

Compounds of Oxygen and Nitrogen.—From the heat of formation of water from atoms

$$2H + O = H_2O(g) + 9.493 \text{ v. e.}$$

the H:O bond is found to have the energy 4.747 v. e. The equation[10]

$$H_2O_2(l) = H_2O(l) + {}^1/_2\,O_2 + 1.02 \text{ v. e.}$$

combined with the heat of vaporization of H_2O_2, 0.50 v. e., leads to

$$2H + 2O = H_2O_2(g) + 10.99 \text{ v. e.}$$

Making use of the postulate of the constancy of bond energies, we subtract 4.75 v. e. for each H:O bond to obtain 1.49 v. e. for the O:O bond.

The $^1\Sigma$ state of the oxygen molecule, 1.62 v. e. above the normal state, probably corresponds to a double bond between the two atoms. This gives 3.47 v. e. for O::O.

From the heat of formation of ammonia, 0.475 v. e., we obtain

$$N + 3H = NH_3 + 11.685 \text{ v. e.}$$

and the value 3.895 v. e. for the N:H bond.

The heats of formation of OF_2 (−0.40 v. e.), NF_3 (1.13 v. e.), Cl_2O (−0.79 v. e.) and NCl_3 (−2.38 v. e.), lead to the values 2.48 v. e. for O:F, 3.29 v. e. for N:F, 2.12 v. e. for Cl:O, and 1.95 v. e. for N:Cl.

Compounds of Carbon.—Heats of combustion of diamond and the aliphatic hydrocarbons show, as was pointed out by Fajans,[11] that the postulate of the constancy of bond energies is not accurate, for assuming that the H:C bond energy is the same in the higher members of the series as in methane, a value for the C:C bond energy is obtained which is 0.2 v. e. lower than that from diamond. It is difficult to decide how to treat this discrepancy. I have arbitrarily chosen to ignore diamond. The values H:C = 4.34 v. e. and C:C = 3.60 v. e. then give good agreement with experiment for the aliphatic hydrocarbons, as is seen by comparing the heats of formation ($E_{obs.}$) of gaseous molecules from atoms as calculated from heats of combustion with the sum of the bond energies ($E_{calcd.}$).

[9] F. L. Arnot, *Nature*, **129**, 617 (1932).

[10] G. L. Matheson and O. Maass, THIS JOURNAL, **51**, 674 (1929).

[11] Fajans, *Ber.*, **53**, 643 (1920); **55**, 2826 (1922); *Z. physik. Chem.*, **99**, 395 (1921).

	$E_{obs.}$, v. e.	$E_{calcd.}$, v. e.		$E_{obs.}$, v. e.	$E_{calcd.}$, v. e.
CH_4	17.37	17.36	C_4H_{10}	54.20	54.20
C_2H_6	29.65	29.64	C_6H_{14}	78.77	78.76
C_3H_8	41.91	41.94	C_7H_{16}	91.00	91.05

Similar calculations for saturated cyclic hydrocarbons show that a three-membered ring is unstable to the extent of over 1 v. e., larger rings showing little strain. The table compares observed heats of combustion with those calculated from bond energies.[12]

		$Q_{obs.}$, v. e.	$Q_{calcd.}$, v. e.	Instability, v. e.
Trimethylene	C_3H_6	21.55	20.49	1.06
Methylcyclobutane	C_5H_{10}	34.31	34.15	0.16
Cyclopentane	C_5H_{10}	34.28	34.15	.13
Methylcyclopentane	C_6H_{12}	41.02	40.98	.04
Cyclohexane	C_6H_{12}	41.02	40.98	.04

Heats of combustion of gaseous hydrocarbons containing double bonds lead to the average value 6.46 v. e. for C::C.

		Q, v. e.	E, v. e.	C::C, v. e.
Ethylene	C_2H_4	14.38	23.84	6.48
Propylene	C_3H_6	21.26	36.07	6.43
Isobutylene	C_4H_8	28.07	48.37	6.45
Trimethylethylene	C_5H_{10}	34.86	60.69	6.49
Diallyl	C_6H_{10}	40.26	66.99	6.40
Hexylene	C_6H_{12}	41.66	73.00	6.52

Heats of combustion for hydrocarbons containing triple bonds are uncertain. Thomsen's values lead to C:::C = 8.68 v. e.

	Q, v. e.	E, v. e.	C:::C, v. e.
Acetylene	13.54	17.28	8.60
Allylene	20.18	29.75	8.79
Dipropargyl	38.30	54.14	8.65

It is interesting to note that the unsaturation of a double bond amounts to 0.74 v. e., this being the energy liberated by a reaction leading to the formation of two carbon–carbon single bonds in place of a double bond. For a triple bond the unsaturation is 2.1 v. e.

Five primary alcohols give an average of 3.56 v. e. for C:O, with a maximum deviation of 0.10 v. e., and six ethers give 3.55 v. e., with a maximum deviation of 0.07 v. e. Secondary and tertiary alcohols seem to be 0.3–0.5 v. e. more stable than corresponds to this C:O value. In view of the agreement between ethers and primary alcohols, we select C:O = 3.55 v. e.

Primary, secondary and tertiary amines give the following values for C:N, Thomsen's values of heats of combustion being used.

[12] The heat of combustion of ethylene oxide, C_2H_4O, combined with C:O = 3.55 v. e., shows the three-membered ring involving oxygen to be unstable to the extent of 0.67 v. e.

	C:N, v. e.		C:N, v. e.
CH_3NH_2	2.82	$(CH_3)_2NH$	2.92
$C_2H_5NH_2$	2.87	$(C_2H_5)_2NH$	2.95
$C_3H_7NH_2$	2.80	$(CH_3)_3N$	2.94

Neglecting the possibility that the bond energy in primary amines be slightly less than in secondary and tertiary amines, we take the average value 2.88 v. e. for C:N.

Cyanogen, acetonitrile and hydrogen cyanide (using Thomsen's value for heats of combustion of the first two) lead to 8.86, 8.98, and 8.74 v. e., respectively, for C:::N. The average of these, 8.86 v. e., is very nearly the mean of C:::C = 8.68 v. e. and N:::N = 9.10 v. e. (in N_2).

Heats of combustion of fluorine-substituted hydrocarbons give C:F = 5.40 v. e. as the average of eight values, maximum deviation 0.35 v. e. Twelve chlorine compounds give an average of 3.41 v. e. for C:Cl. The same value is obtained from the heat of formation of CCl_4. Three bromine compounds (heats of combustion from Thomsen) give C:Br = 2.83 v. e., and two iodine compounds, CH_3I and C_2H_5I (Thomsen), give C:I = 2.2 v. e. The last two values are uncertain. Other data, obtained by Berthelot and by Roth and Macheleldt and quoted by Swietoslawski,[13] give the value 2.45 v. e. for C:I.

Bond Energies and the Relative Electronegativity of Atoms.—In Table II there are collected the energies of single bonds obtained in the preceding sections. One additional value, obtained by a method to be described later, is also included: 1.44 v. e. for N:N. Under each bond energy is given the value for a normal covalent bond, calculated from additivity, and below that the difference Δ. It is seen that Δ is positive in twenty of the twenty-one cases. The exception, C:I, may be due to experimental error, and be not real.

Regularities observed in the Δ-values suggest that it is possible to make a rough assignment of the atoms to positions along a scale representing degree of electronegativity, with the assumption that Δ is a function of the linear separation of the loci of the two atoms on the scale, in the way that genes are mapped in a chromosome from crossover data. It is to be observed that the values of $\Delta^{1/2}$ are approximately additive (these values are given directly below those of Δ). For example, the sum of $\Delta^{1/2}$ for H:A and A:F is 2.05, 2.06, 1.91, and 2.06 for A = C, N, O, and Cl, respectively. We accordingly write

$$\Delta_{A:B} = (x_A - x_B)^2 \qquad (1)$$

with Δ measured in volt-electrons, and construct the scale shown in Figs. 3 and 4 on this basis. The reliability of the method is indicated by Fig. 3, in which four distinct procedures are illustrated. The coördinates of the elements on this scale are given in Table III.

[13] W. Swietoslawski, "Thermochemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928.

TABLE II

	H	C	N	O	F	Cl	Br	I
H	4.44	4.34	3.89	4.75	6.39	4.38	3.74	3.07
		4.02	2.94	2.99	3.62	3.45	3.20	2.99
		0.32	0.95	1.76	2.77	0.93	0.54	0.08
		.57	.98	1.33	1.67	.97	.74	.28
	C	3.60	2.88	3.55	5.40	3.41	2.83	2.45
			2.52	2.55	3.20	3.03	2.78	2.57
			0.36	1.00	2.20	0.38	0.05	−0.12
			.60	1.00	1.48	.62	.22	
		N	1.44		3.29	1.95		
					2.12	1.95		
					1.17	0.00		
					1.08	.00		
			O	1.49	2.48	2.12		
					2.15	1.98		
					0.33	0.14		
					.58	.37		
Observed bond energy				F	2.80	3.82		
Normal covalent bond energy						2.63		
Δ						1.19		
$\Delta^{1/2}$						1.09		
					Cl	2.468	2.231	2.143
							2.215	2.001
							0.016	0.142
							.13	.38
						Br	1.962	1.801
								1.748
								0.053
								.23
							I	1.535

TABLE III

COÖRDINATES OF ELEMENTS ON THE ELECTRONEGATIVITY SCALE

H	0.00	Br	0.75
P	.10	Cl	.94
I	.40	N	.95
S	.43	O	1.40
C	.55	F	2.00

These coördinates, introduced in Equation 1, lead to values of Δ which agree with those of Table II with an average error of 0.09 v. e., excluding H:F. The calculated Δ for H:F is 4.00 v. e., 1.23 v. e. higher than observed; this indicates that Equation 1 is inaccurate when $x_A - x_B$ becomes as large as 2.

The electronegativity map may be used with considerable confidence in predicting bond energies, especially for atoms which lie near each other on the map. It will be observed that the difference in bond energy of H:A and

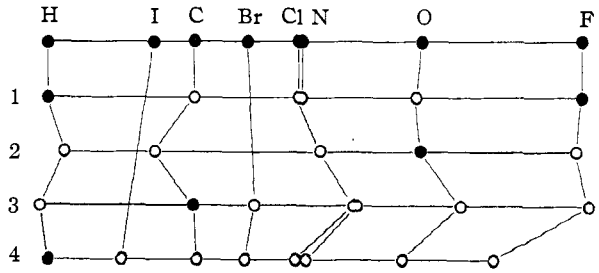


Fig. 3.—The construction of the electronegativity map. Map loci of atoms were obtained by the use of values of $\Delta^{1/2}$ relative to the atoms represented by solid circles: (1) loci taken to give the correct ratio of $\Delta^{1/2}$ for H:A and A:F. Absolute values of $\Delta^{1/2}$ are shown in the other lines, for (2) A:O, (3) C:A and (4) H:A.

A:F increases rapidly in the order A = C, Cl, O. Now the value of this difference for N is only slightly greater than for Cl, showing that the locus of N on the map should lie just to the right of that for Cl, and that in

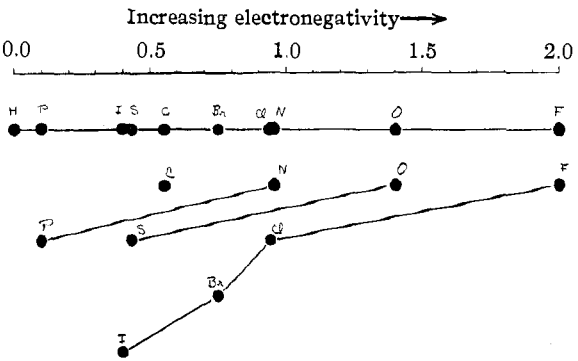


Fig. 4.—Map representing the relative degree of electronegativity of atoms.

consequence $\Delta = 0.00$ for N:Cl. The bond energies for N:Cl and Cl:Cl then lead to 1.44 v. e. for N:N, the value given in Table II. This value could be checked if the heat of formation of gaseous hydrazine were known. The predicted value is

$$N_2 + 2H_2 = N_2H_4(g) - 0.96 \text{ v. e.}$$

It may be mentioned that the heats of combustion of hydrazobenzene and azobenzene give 1.59 v. e. for N:N and 4.24 v. e. for N::N, with rather large probable errors.

From the equations

$$S(g) = S_{rhombic} + 2.89 \text{ v. e.}$$
$$S_{rh.} + Cl_2 = SCl_2(g) + 0.34 \text{ v. e.}$$
$$S_{rh.} + H_2 = H_2S + 0.23 \text{ v. e.},$$

we obtain S:Cl = 2.85 v. e. and H:S = 3.78 v. e. From

$$2S_{rh.} + Cl_2 = S_2Cl_2(g) + 0.24 \text{ v. e.}$$

we obtain, with the use of the above S:Cl value, S:S = 2.79 v. e. in S_2Cl_2. The equation

$$^1/_8\, S_8(g) = S_{rh.} + 0.11 \text{ v. e.}$$

gives S:S = 2.78 v. e., if the S_8 molecule consists of an eight-membered ring involving eight single bonds; the agreement with the S_2Cl_2 value provides strong support for this structure. From these energy values the map position of sulfur was obtained.

The S_6 molecule, supposed to contain six single bonds, is less stable than expected by 0.30 v. e., presumably because of steric effects.

From the trend of map loci with position in the periodic table phosphorus may be placed very near hydrogen on the map, perhaps at about 0.10. This requires Δ to be very small (0.01 v. e.) for H:P. From

$$^1/_4\, P_4(g) + {}^3/_2\, H_2(g) = PH_3(g) + 0.246 \text{ v. e.}$$

we obtain P:H = 2.302 v. e. + C, in which C is one-third of the energy of dissociation of $^1/_4\, P_4(g)$ into P(g). This then gives, with Δ = 0.01 v. e., the value 0.14 v. e. + $2C$ for P:P. P_4 presumably has a tetrahedral structure, with single bonds at 60° angles;[14] the bonds are 0.14 v. e. weaker than normal P:P bonds, as compared with 0.05 v. e. for S:S bonds in S_6.

The equation

$$^1/_4\, P_4(g) + {}^3/_2\, Cl_2 = PCl_3(g) + 3.30 \text{ v. e.}$$

gives P:Cl = 2.41 v. e. + C.

The extent to which Equation 1 is valid and the accuracy of the map are graphically shown in Fig. 5. The vertical lines, representing Δ-values, should increase in height with the square of their distance from the diagonal.

It is evident that the map and Equation 1 can be used for the prediction of the energies of bonds for which no experimental data are available, the values being trustworthy to about 0.05 v. e. for map distances less than 0.50, and 0.1–0.2 v. e. for distances up to 1 or 1.5. Table IV contains predicted values, with the aid of which heats of formation of purely covalent compounds containing single bonds, such as SF_2 (but not SF_6), can be calculated. In some cases all data needed for testing these values are available except heats of vaporization or sublimation. Thus the heat of formation of $S_2Br_2(l)$, 0.09 v. e., agrees with the bond energies if the heat of vaporization of S_2Br_2 be 0.44 v. e., which is a not unreasonable value (that for Br_2 being 0.33 v. e.). The somewhat doubtful value 0.0 v. e. reported

[14] R. Hultgren, *Phys. Rev.*, **40**, 891 (1932).

for the heat of formation of $S_2I_2(c)$ leads to a heat of sublimation of 0.9 v. e. (that for I_2 being 0.65 v. e.). Similarly the heats of formation of $PBr_3(l)$,

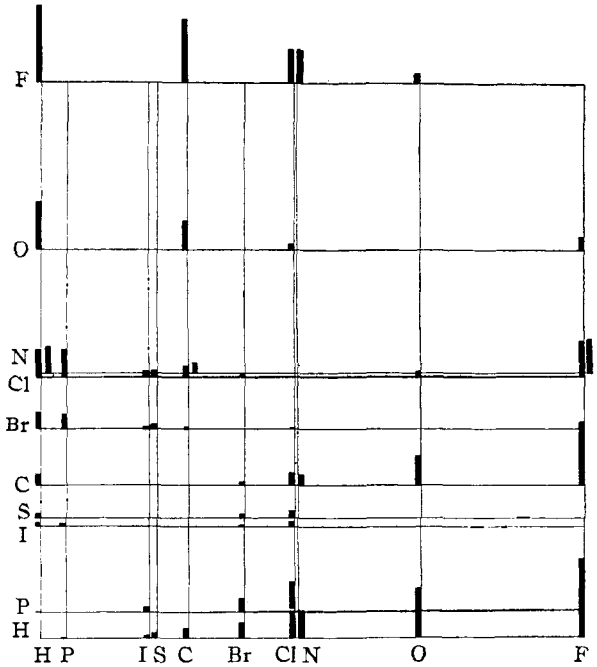


Fig. 5.—In this figure ordinates and abscissas represent loci on the electronegativity map, and the heavy vertical lines are drawn to the height Δ, the observed deviation from additivity of bonds, attributed to their ionic character. Equation 1 in the text requires that these heights increase with the square of the distance from the diagonal.

1.97 v. e., and $PI_3(c)$, 0.48 v. e., lead to the reasonable values 0.51 v. e. and 0.98 v. e. for the heat of vaporization of PBr_3 and the heat of sublimation of PI_3, respectively.

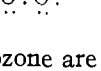
TABLE IV

PREDICTED BOND ENERGIES

N:O	1.67 v. e.	S:N	2.38 v. e.
Br:N	1.74	S:O	3.08
I:N	1.79	S:F	5.25
Br:O	2.15	P:I	0.93 + C
I:O	2.52	P:S	1.56 + C
Br:F	3.94	P:C	3.17 + C
I:F	4.72	P:Br	1.47 + C
I:S	2.16	P:N	1.51 + C
S:C	3.20	P:O	2.50 + C
S:Br	2.47	P:F	5.08 + C

Assuming that the energy of formation of crystalline silicon (with the diamond structure) is the energy of the Si:Si bonds, the heats of formation 15.70 and 6.20 v. e. of gaseous SiF_4 and $SiCl_4$ lead to values of 1.98 and 1.24 for $\Delta^{1/2}$ for Si:F and Si:Cl, respectively. These substantiate the map position of about -0.15 obtained by extrapolating the series Cl, S, P. This and many other map positions which could be similarly obtained are not included in Fig. 4 and Table III, however, because of the somewhat greater uncertainty attached to them. With this map position, the heat of formation of SiH_4 should be about 0.08 v. e., or less if the metallic character of crystalline silicon makes some contribution to its energy. The value 0.5 v. e. given in "International Critical Tables" is without doubt too large; Landolt–Börnstein reports -0.29 v. e.

Arsenic, antimony, selenium, and tellurium no doubt lie close to hydrogen on the map, so that single-bond energies can be obtained for them from the heats of formation of hydrides, as in the case of phosphorus, by assuming Δ to be very small. Crystals of selenium and tellurium contain long spiral strings, in which each atom is presumably held to two others by covalent bonds, and those of arsenic and antimony contain layers, in which each atom is presumably similarly attached to three others. With $\Delta_{M:H}$ very small, the heat of reaction of such a string or layer with hydrogen should be nearly zero, so that the observed negative heats of reaction for the crystals give just the energy necessary to separate the strings or layers in the crystals. This energy is, per atom, 1.08 v. e. for selenium, 1.52 v. e. for tellurium, 1.92 v. e. for arsenic, and 1.5 v. e. for antimony, the last value being probably too low because of error in the reported heat of formation of the hydride.

The observed value of the heat of formation of O_4 from atoms, 10.19 v. e., is so much greater than the energy of four O:O bonds, 5.96 v. e., that the structure  for this molecule must be rejected. The corresponding values for ozone are 6.15 v. e. and 4.47 v. e., causing the structure  to be rejected also. Ozone probably has a structure like that of SO_2, as suggested by Lewis. The very small heat of formation of O_4 from $2O_2$ and the ease with which dissociation occurs (even crystalline oxygen showing some paramagnetism) indicate that O_4 consists of two $^3\Sigma O_2$ molecules held together loosely by van der Waals forces, the exchange terms being larger for two triplet molecules combining to a singlet than they are for singlet molecules.

The metallic elements may also be roughly located on the map, though the significance and usefulness of their map positions is not so great as for the non-metals.

The property of electronegativity discussed in this paper and defined by Equation 1 is not analogous to the electron affinity of atoms, but is closely related to the intuitive conception of electronegativity possessed by the chemist. The relation to the periodic system is the expected one. Fluorine and oxygen are by far the most electronegative atoms, with fluorine much more electronegative than oxygen. The series C, N, O, F is almost uniform. Fluorine is much more electronegative than the other halogens, and deserves to be classed by itself as a superhalogen. OF_2 should be called oxygen fluoride, and Cl_2O chlorine oxide, the more electronegative element being written last. In nitrogen trichloride, NCl_3, nitrogen and chlorine are neither positive nor negative, the bonds being normal covalent bonds, and the molecule the best example of a normal covalent molecule that we have, other than the symmetrical molecules. Nitrogen trichloride would decompose into gaseous elementary molecules with no heat effect if elementary nitrogen contained single N:N bonds. Since the triple bond in N_2 is 4.78 v. e. more stable than three N:N bonds, half this energy quantity, 2.39 v. e., is emitted during the decomposition of NCl_3. The contribution of ionic terms, giving $\Delta = 1.17$ v. e., overcomes this for NF_3, and leads to a positive heat of formation.

Summary

After the discussion and definition of extreme ionic bonds and normal covalent bonds, values of the energy of twenty-one single bonds are obtained from experimental values of heats of formation and combustion of gaseous molecules, with the use of the assumption that the energy of formation from separated atoms of a molecule to which a single Lewis electronic structure can be assigned is the sum of constant terms representing the various bonds. The postulate of the additivity of the energies of normal covalent bonds is then formulated, and it is found that deviations from additivity, Δ, are positive for all bonds (with one doubtful exception), and increase as the ionic character of the bond increases. An assignment of atoms to positions on a map representing relative degree of electronegativity is then made with the use of the Δ-values, according to the equation $\Delta_{A:B} = (x_A - x_B)^2$, where x_A and x_B represent the coördinates of atoms A and B on the map. Values of the energy of twenty bonds for which experimental data are not available are predicted by means of this equation, and a number of questions regarding the structure of molecules are discussed.

PASADENA, CALIFORNIA