

Molecular Constants and Chemical Theories I. The Parachor (Molecular Volume)

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Molecular Constants and Chemical Theories*

I. The Parachor (Molecular Volume)

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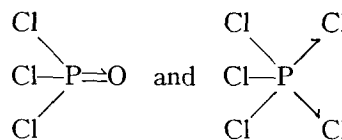
Theories of valency are based on physical properties of molecules, most of which are expressed in terms of so-called "additive molecular constants." Dipole moments, molecular volumes, bond distance, energies of formation, etc., belong to this class. The following paper intends to show that such constants are capable of being consistently interpreted in various entirely different ways. Hence a number of entirely equivalent but different and discordant theories of valency are possible, leading, for instance, to classical or to resonance structures of inorganic molecules. The choice between them therefore is arbitrary and not due to necessity. In the following part, I, one of these additive molecular constants, namely, the molecular volume in terms of the parachor, is studied in detail. The existence of coordinate types of covalent linkage having been ruled out by new experimental evidence for many inorganic first-order molecules formed by a definite central atom (Section 1), a new set of atomic parachors is calculated on

the basis of the classical formulae of chemistry (Section 2). Instead of resorting to different types of bonds and their respective parachor constants, it ascribes different constants to the same atom in different valence states (Section 3). The contributions of the constituent atoms to the volume of the covalent molecule thus calculated bear a close relation to their atomic numbers and to their ionization potentials (Section 4). The new atomic parachors account for such molecules as N_2 , O_2 , N_2O , CO , CO_2 , SO_2 , which earlier had to be considered as anomalous, and also give the correct structure of the azides. However, as the molecular volume apparently can be separated into atomic contributions according to entirely different concepts of valency, the parachor (i.e., the molecular volume) is an example of an additive molecular constant which is unable to distinguish between different possible structures of a molecule or the different conflicting chemical theories on which they are based.

1. INTRODUCTION

THE parachor was originally introduced by Sugden¹ as an additive and constitutive molecular constant which permits a comparison of atomic and molecular volumes in a convenient way. As with other similar molecular constants it was found soon not to lead to strictly additive operations but to be influenced by a number of constitutive factors as well. In particular, the molecular parachor of a molecule such as PCl_3 having been separated into contributions of the constituent atoms, it is not possible to reconstruct the molecular parachor of a molecule like PCl_5 or $POCl_3$ by adding up these atomic parachors. This happens whenever atomic parachors are calculated from a molecule formed by a central atom in its lower state of valency, and are applied to another one the central atom of

which is in a higher valence state. Consequently these differences have been ascribed by Sugden to differences of linkage, such molecules having been formulated as



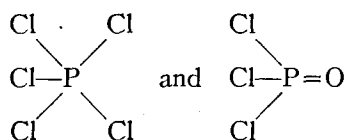
with semipolar double bonds and singlet linkages.* This interpretation of the parachor has at times greatly contributed to the acceptance of these types of linkages into chemical theories. Its influence can still be felt in those wave mechanical theories of valency in which these types of linkages are represented as enhanced resonance of covalent and ionic parent structures.

* The following paper in both its parts originates in a course of lectures on "chemical physics" which the author delivered last winter as visiting professor of The Illinois Institute of Technology. In the chapter on additive molecular constants, some of these were recalculated in order to compare their working and interdependence from the viewpoint of a uniform concept of chemical linkage. Some of the results are communicated here.

¹ S. Sugden, *The Parachor and Valency* (London, 1930), and references therein.

* The half-barb symbols \rightrightarrows and \rightarrow are used throughout this paper to indicate semipolar double bonds and singlet linkages, respectively, while the arrow \rightarrow is retained for dipole moments. Sugden's symbol $[P]$ is occasionally used for parachor values. The parachor is defined by $[P] = MT^{1/4}/D - d$ (M = mol. weight, T = surface tension, D and d = the densities of liquid and vapor phase, respectively). Comparison of $[P]$ values of different molecules amount to a comparison of molecular volumes at constant surface tension.

However, an entirely different interpretation of this constant is also possible. In the above example the atomic parachor of phosphorus is kept constant and variations are introduced for the bond. Instead, the bond constants may be kept constant and different parachors used for phosphorus in its tri- and pentavalent state. Such a procedure is common practice for molecular refractivities, and Hunter and Samuel² have shown that a similar system of atomic parachors may be developed in which exactly the same additivity obtains.* This procedure of course leads directly to the older structural formulae like



which do not recognize different varieties of the non-electrostatic bond. The authors confined themselves to a few examples of typical molecules, as at that time they merely wished to show that the parachor does not provide diagnostic information as to different varieties of covalent linkages.

Precisely for this type of molecules formed by a marked central atom which may exist in two or more different states of valency, Sutton and his collaborators³ have recently provided the final argument. The bond moments such as $\text{P} \rightarrow \text{O}$, $\text{P} \rightarrow \text{S}$, or $\text{S} \rightarrow \text{O}$ taken in conjunction with atomic distances from electron diffraction measurements are by far too small for semipolar double bonds, and they conclude that ordinary double bonds have to be reintroduced for such structures.** As has been shown earlier⁴ in reality there does not exist a sufficient experimental basis for the concept of coordinate bonds for molecules of this type and spectroscopical results appear to be incompatible with it. These

² R. F. Hunter and R. Samuel, *Rec. Trav. Chim.* **54**, 114 (1935); *Chem. and Ind.* **54**, 31, 467, 635 (1935).

* Conversely, it is entirely possible to rewrite the theory of molecular refractivities with one constant only per atom and different constants for the bonds.

³ L. E. Sutton, *Ann. Repts.* **37**, 74 ff. (1940) and references therein.

** Difficulties inherent in the calculation of bond moments may render this conclusion not entirely inevitable in some cases, yet it certainly holds for a molecule such as SO_2 ; cf. Part II of this paper.

⁴ R. F. Hunter and R. Samuel, *Nature* **138**, 411 (1936) and references therein.

new results directly disclose the absence of such bonds in the most typical molecules. At the same time, as Sugden's system of atomic parachor constants is workable only with this difference of linkage, this new experimental evidence deprives it of its physical basis.

As this is the situation, two avenues of investigation suggest themselves for obvious reasons. Provided comparison of atomic and molecular volumes by means of the parachor (i.e., the molecular volume) are not to be abandoned entirely as a source of information on molecular structures, the alternative system of interpretation workable without resort to semipolar double bonds has to be fully developed. Secondly, the empirical and theoretical evidence has to be examined with a view to determining whether the results of such a procedure are compatible with conclusions on molecular structures reached in related fields.

In Part I of this communication, new additive values for atomic parachor are calculated under the assumption of different values for different valence states of the same atom but with only one variety of covalent linkage. An entirely consistent system results which, however, can be based only on the classical structural formulae of chemistry. In this first part they are taken for granted, including the pentacovalency of nitrogen, as the only means left to obtain additivity of the atomic parachors, i.e., the contribution of the constituent atoms towards the volume of the molecule. The more detailed study of the parachor, however, should be considered as a model only. In a shorter review of other molecular constants such as dipole moments, bond energies, or bond distances, it will be shown in Part II that similar systems of additive constants based on the classical structures, are entirely workable for all of them. For molecules (of Werner's first order) formed by a definite central atom, the older classical formulae including pentacovalency of nitrogen, will be seen to be entirely compatible with the wave mechanical representation of valency. The contributions of ionic parent structures will emerge as much smaller than sometimes thought, and of the same order for ordinary covalent as well as for the so-called coordinate bonds. From the very definite result that any additive molecular constant may be separated

into additive atomic increments according to different systems of structures and according to different chemical concepts, one definite conclusion can be drawn, namely, that none of them is able to distinguish between different chemical theories. This reduces the experimental basis for some of them, and therefore it becomes quite likely that the classical structures, taken for

granted in Part I, indeed are the nearest approach to reality.

2. CALCULATION OF ATOMIC PARACHORS

The results of a calculation of atomic parachors are listed in Table I. They are the contributions made by the individual atoms to the parachor of a covalent molecule. The separation of molecular into atomic parachors is then confirmed or justified by Table II, in which the observed parachors of a number of typical molecules are compared with those calculated by means of the new values of Table I as well as with those calculated according to Sugden's method.

Table I is almost self-explanatory, and only a few remarks on some details of the calculations are necessary. The values of C and H calculated by Sugden from the increase of the parachor per CH_2 group in various homologous series can be accepted as the basis for any separation of molecular parachors into contributions of the constituent atoms. In the same way the proposed change in the method of calculation cannot affect such of Sugden's values as are derived from those of C and H directly and by means of simple structural formulae. These include the halogen atoms (from simple aliphatic compounds), the tetravalent atoms of the fourth group based on measurements of the tetrahydrides of Si, Ge, Sn, and Pb,⁵ respectively, and those of the trivalent atoms As, Sb, Bi, and B, taken from halogenides MX_3 . They are included in Table III.

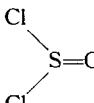
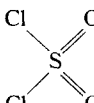
For the increase of the parachor produced by a double or triple bond, we accept Sugden's value as far as the C atom is concerned, i.e., the atomic parachors of 4.8 for $>\text{C}<$, $4.8 + 23.2 = 28.0$ for $>\text{C}=\text{C}<$, and $4.8 + 46.6 = 51.4$ for $-\text{C}\equiv\text{C}-$.*

However, the increase per double bond changes with different atoms, and Sugden introduced already a special value for the carboxyl group. In the present system no attempt has been made to

⁵ Corrected values of D. T. Lewis, J. Chem. Soc., p. 1056 (1938).

* Sugden's increment of 46.6 for the triple bond is an average for substances containing both the groups $-\text{C}\equiv\text{C}-$ and $-\text{C}\equiv\text{N}$. For the former the empirical value appears to be lower, i.e., 44.8 in $\text{HC}:\text{CH}$ or 40.1 in $\text{CH}_3:\text{C}:\text{CH}$, and for the CN group it will be lowered by the new and slightly higher parachor of N. Hence the final value will be rather nearer 44 than 47.—The value of 23.2 for the carbon double bond will also be used for divalent carbon in isocyanides. Small improvements of additivity might be obtained in these two directions, as also for O in carbonyl and carboxyl groups.

TABLE I. Calculation of atomic parachors.*
(The superscripts indicate the state of valency in covalent linkage, not an ionic charge.)

Molecule	Molecular parachor	Atomic symbol	Atomic parachor	Remarks
1. $(\text{C}_2\text{H}_5)_2\text{O}$	$\begin{Bmatrix} 211.7 \\ 209.5 \end{Bmatrix}$	$-\text{O}-$	20.5	*
2. $\text{O}=\text{C}=\text{O}$	77.5	$=\text{O}$	36.4	*
3. $\text{C}=\text{O}$	61.6	C^2	28.4	*
4. $\text{S}=\text{C}=\text{S}$	144.1	$=\text{S}^2$	69.7	*
5. $\text{C}_2\text{H}_5-\text{S}-\text{H}$	$\begin{Bmatrix} 257.5 \\ 256.4 \end{Bmatrix}$	$-\text{S}^2-$	49.8	
6. 	174.5	S^4	29.5	*
7. 	195.3	S^6	13.9	*
8. $\text{S}=\text{C}=\text{Se}$	156.4	$=\text{Se}^2$	81.9	
9. $(\text{C}_6\text{H}_5)_2\text{Se}$	445.6	$-\text{Se}^2-$	65.6	
10. $(\text{C}_6\text{H}_5)_2\text{SeO}$	461.6	Se^4	45.2	
11. $(\text{C}_6\text{H}_5)_2\text{Te}$	457.4	$-\text{Te}^2-$	77.4	
12. $(\text{Et}\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2\text{Te}_2$	723.0	$=\text{Te}^2$	87.7	
13. $(\text{C}_6\text{H}_5)_2\text{TeCl}_2$	547.3	Te^4	58.7	
14. NOCl	108.1	$>\text{N}^3-$	17.4	**
15. $(\text{C}_6\text{H}_5)-\text{N}^3=\text{N}^3=\text{N}^3$	267.3	$=\text{N}^3-$	32.6	
16. $\text{N}\equiv\text{N}$	60.4	$\equiv\text{N}^3$	43.0	
17. $(\text{C}_6\text{H}_5)\text{NO}_2$	264.5	N^5	1.7	
18. PCl_3	$\begin{Bmatrix} 201.1 \\ 199.0 \end{Bmatrix}$	P^3	37.1	
19. $\text{Cl}_3\text{P}=\text{O}$	217.6	P^5	18.3	
20. SbCl_5	311.8	Sb^5	40.3	
21. SnCl_2	183.8	Sn^2	75.2	
22. PbCl_2	194.5	Pb^2	85.9	

* Similar values used already by Hunter and Samuel, reference 2.

** N is the positive partner and the constant of the double bond therefore included in the increment of oxygen. Values derived from amines are similar but show slight variations.

TABLE II. Observed and calculated molecular parachor.

Substance	[P] ob- served	New calculation		[P] calcu- lated	Calculation after Sugden	
		[P] calcu- lated	Formula used		[P] calcu- lated	Formula used
<i>A. Sulphur compounds</i>						
1. Sulphur dioxide	101.5	102.3	$\text{O}=\text{S}^4=\text{O}$	109.8	$\text{O}=\text{S}^2=\text{O}$	
2. Sulphur chloride	204.3	205.6	$\begin{array}{c} \text{Cl} \\ \\ \text{S}^2=\text{S}^4 \\ \\ \text{Cl} \end{array}$	205.0	$\begin{array}{c} \text{Cl} \\ \\ \text{S}=\text{S} \\ \\ \text{Cl} \end{array}$	
3. Ethyl sulphite	299.7	297.1	$(\text{EtO})_2\text{S}^4=\text{O}$	298.4	$(\text{EtO})_2\text{S}^2=\text{O}$	
4. Ethyl toluene sulphinate	410.3	410.5	$\begin{array}{c} \text{C}_7\text{H}_7 \\ \\ \text{S}^4=\text{O} \\ \\ \text{EtO} \end{array}$	410.7	$\begin{array}{c} \text{C}_7\text{H}_7 \\ \\ \text{S}=\text{O} \\ \\ \text{EtO} \end{array}$	
5. Ethyl ethane sulphonate	295.8	297.4	$\begin{array}{c} \text{EtO} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S}^6 \\ \diagup \quad \diagdown \\ \text{Et} \quad \text{O} \end{array}$	298.4	$\begin{array}{c} \text{OEt} \\ \\ \text{O}=\text{S}^2=\text{O} \\ \\ \text{Et} \end{array}$	
6. Methyl sulphate	238.9	239.9	$\begin{array}{c} \text{MeO} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S}^6 \\ \diagup \quad \diagdown \\ \text{MeO} \quad \text{O} \end{array}$	240.2	$\begin{array}{c} \text{OMe} \\ \\ \text{O}=\text{S}^2=\text{O} \\ \\ \text{OMe} \end{array}$	
7. Diphenyl sulphone	465.7	466.9	$\begin{array}{c} \text{Ph} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S}^6 \\ \diagup \quad \diagdown \\ \text{Ph} \quad \text{O} \end{array}$	465.1	$\begin{array}{c} \text{Ph} \\ \\ \text{O}=\text{S}^2=\text{O} \\ \\ \text{Ph} \end{array}$	
8. Methyl toluyl sulphone	369.8	370.2	$\begin{array}{c} \text{C}_7\text{H}_7 \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S}^6 \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{O} \end{array}$	370.2	$\begin{array}{c} \text{C}_7\text{H}_7 \\ \\ \text{O}=\text{S}^2=\text{O} \\ \\ \text{Me} \end{array}$	
9. Ethyl toluene sulphonate	431.8	431.3	$\begin{array}{c} \text{C}_7\text{H}_7 \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{EtO} \quad \text{O} \end{array}$	429.2	$\begin{array}{c} \text{C}_7\text{H}_7 \\ \\ \text{O}=\text{S}^2=\text{O} \\ \\ \text{OEt} \end{array}$	
10. Toluene sulphonyl chloride	367.8	370.0	$\begin{array}{c} (\text{C}_7\text{H}_7) \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S}^6 \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{O} \end{array}$	368.4	$\begin{array}{c} \text{C}_7\text{H}_7 \\ \\ \text{O}=\text{S}^2=\text{O} \\ \\ \text{Cl} \end{array}$	
11. *Sulphuric acid— from to	144.8 152.3	150.3	$\begin{array}{c} \text{H}-\text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S}^6 \\ \diagup \quad \diagdown \\ \text{H}-\text{O} \quad \text{O} \end{array}$	147.6	$\begin{array}{c} \text{O}-\text{H} \\ \\ \text{O}=\text{O}^2=\text{O} \\ \\ \text{O}-\text{H} \end{array}$	
<i>B. Selenium and tellurium compounds</i>						
12. Phenyl selenium bromide	321.4	323.6	$\text{Ph}-\text{Se}^2-\text{Br}$	320.5	$\text{Ph}-\text{Se}-\text{Br}$	
13. Diphenyl diselenide	506.5	506.5	$\text{Ph}-\text{Se}^2-\text{Se}^2-\text{Ph}$ or	505.0	$\text{Ph}-\text{Se}-\text{Se}-\text{Ph}$	
	506.5		$\begin{array}{c} \text{Ph} \\ \\ \text{Se}^4=\text{Se}^2 \\ \\ \text{Ph} \end{array}$			

* Calculated with Mumford and Phillips value of 11.3 for H in OH. Cf. reference 6.

TABLE II.—Continued.

Substance	[P] observed	New calculation		Calculation after Sugden	
		[P] calculated	Formula used	[P] calculated	Formula used
14. Selenium oxychloride	181.1	190.2	$\text{Cl}_2=\text{Se}^4=\text{O}$	189.5	$\text{Cl}_2=\text{Se}=\text{O}$
15. *Selenium oxychloride hydrate	222.8	217.4	$\begin{array}{c} \text{Cl} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{Se}^4 \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{OH} \end{array}$	208.9	$\begin{array}{c} \text{Cl} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{Se} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{OH} \end{array}$
16. *Phenyl selenious acid	299.5	303.4	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{Se}^4=\text{O} \\ \diagup \\ \text{HO} \end{array}$	302.2	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{Se}=\text{O} \\ \diagup \\ \text{HO} \end{array}$
17. Dibutyl telluride	426.8	430.0	$(\text{C}_4\text{H}_9)_2\text{Te}^2$	425.6	$(\text{C}_4\text{H}_9)_2\text{Te}$
18. Dimethyl tellurous dichloride	282.5	279.5	$\text{Me}_2\text{Te}^4\text{Cl}_2$	275.4	$\begin{array}{c} \text{Cl} \\ \diagup \\ \text{Me}_2\text{Te} \\ \diagdown \\ \text{Cl} \end{array}$
<i>C. Phosphorus compounds</i>					
19. Phosphorus tribromide	242.9	241.1	$\begin{array}{c} \text{Br} \\ \diagup \\ \text{Br}-\text{P}^3 \\ \diagdown \\ \text{Br} \end{array}$	241.7	$\begin{array}{c} \text{Br} \\ \diagup \\ \text{Br}-\text{P} \\ \diagdown \\ \text{Br} \end{array}$
20. Triphenyl phosphine	607.7	607.1	$\begin{array}{c} \text{Ph} \\ \diagup \\ \text{Ph}-\text{P}^3 \\ \diagdown \\ \text{Ph} \end{array}$	607.7	$\begin{array}{c} \text{Ph} \\ \diagup \\ \text{Ph}-\text{P} \\ \diagdown \\ \text{Ph} \end{array}$
21. Phenyl phosphate	686.5	686.2	$(\text{PhO})_3\text{P}^5=\text{O}$	686.1	$(\text{PhO})_3\text{P}=\text{O}$
22. Ethyl phosphate	399.1	401.5	$(\text{EtO})_3\text{P}^5=\text{O}$	401.4	$(\text{EtO})_3\text{P}=\text{O}$
23. Phosphorus pentachloride	282.5	289.8	$\begin{array}{c} \text{Cl} \\ \diagup \\ \text{Cl}_3\text{P}^5 \\ \diagdown \\ \text{Cl} \end{array}$	284.0	$\begin{array}{c} \text{Cl} \\ \diagup \\ \text{Cl}_3\text{P} \\ \diagdown \\ \text{Cl} \end{array}$
<i>D. Compounds of trivalent nitrogen</i>					
24. Dimethyl nitrosamine	183.4	183.4	$\text{Me}_2=\text{N}^3-\text{N}^3=\text{O}$	180.4	$\text{Me}_2=\text{N}-\text{N}=\text{O}$
25. Diethyl nitrosamine	260.3	261.4	$\text{Et}_2=\text{N}^3-\text{N}^3=\text{O}$	258.4	$\text{Et}_2=\text{N}-\text{N}=\text{O}$
26. Methyl phenyl nitrosamine	313.6	317.3	$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{N}^3-\text{N}^3=\text{O} \\ \diagup \\ \text{Ph} \end{array}$	314.6	$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{N}-\text{N}=\text{O} \\ \diagup \\ \text{Ph} \end{array}$
27. Acetamide	148.0	148.9	$\begin{array}{c} \text{H} \\ \diagup \\ \text{Me}-\text{CO}-\text{N}^3 \\ \diagdown \\ \text{H} \end{array}$	150.8	$\begin{array}{c} \text{H} \\ \diagup \\ \text{Me}-\text{CO}-\text{N} \\ \diagdown \\ \text{H} \end{array}$
28. Butyl nitrite	251.8	247.4	$\text{C}_4\text{H}_9-\text{O}-\text{N}^3=\text{O}$	248.8	$\text{C}_4\text{H}_9-\text{O}-\text{N}=\text{O}$
29. Amyl nitrite	287.4	286.4	$\text{C}_5\text{H}_{11}-\text{O}-\text{N}^3=\text{O}$	287.8	$\text{C}_5\text{H}_{11}-\text{O}-\text{N}=\text{O}$
30. Ethyl isothiocyanate	211.7	210.2	$\text{Et}-\text{N}^3=\text{C}=\text{S}$	207.2	$\text{Et}-\text{N}=\text{C}=\text{S}$
31. Phenyl isothiocyanate	304.8	305.1	$\text{Ph}-\text{N}^3=\text{C}=\text{S}$	301.9	$\text{Ph}-\text{N}=\text{C}=\text{S}$
32. Aceto nitrile	122.2	122.3	$\text{CH}_3-\text{C}\equiv\text{N}^3$	120.0	$\text{CH}_3-\text{C}\equiv\text{N}$

TABLE II.—Continued.

Substance	[P] ob- served	New calculation		Calculation after Sugden	
		[P] calcu- lated	Formula used	[P] calcu- lated	Formula used
33. Hydrogen cyanide	81.5	83.3	$\text{H}-\text{C}\equiv\text{N}^3$	81.0	$\text{H}-\text{C}\equiv\text{N}$
34. Ethyl thiocyanate	$\begin{Bmatrix} 210.7 \\ 209.1 \end{Bmatrix}$	211.1	$\text{C}_2\text{H}_5-\text{S}-\text{C}\equiv\text{N}^3$	207.2	$\text{C}_2\text{H}_5-\text{S}-\text{C}\equiv\text{N}$
35. Methyl isocyanide	122.1	125.1	$\text{CH}_3-\text{N}^3=\text{C}^2$	118.4	$\text{CH}_3-\text{N}\equiv\text{C}$
36. Ethyl isocyanide	163.8	164.1	$\text{C}_2\text{H}_5-\text{N}^3=\text{C}^2$	157.4	$\text{C}_2\text{H}_5-\text{N}\equiv\text{C}$
<i>E. Compounds of pentavalent nitrogen</i>					
37. Nitrous oxide	81.1	81.1	$\text{N}^3\equiv\text{N}^5=\text{O}$	89.8	$\text{N}\equiv\text{N}=\text{O}$
38. Nitro methane	132.0	130.6	$\text{CH}_3-\text{N}^5\begin{array}{c} \text{O} \\ // \\ \text{O} \end{array}$	130.2	$\text{CH}_3-\text{N}=\text{O}$ $\text{O}=\text{N}=\text{O}$
39. Nitro ethane	171.2	169.6	$\text{C}_2\text{H}_5-\text{N}^5\begin{array}{c} \text{O} \\ // \\ \text{O} \end{array}$	169.2	$\text{C}_2\text{H}_5-\text{N}=\text{O}$ $\text{O}=\text{N}=\text{O}$
40. Ethyl nitrate	189.6	190.1	$\text{C}_2\text{H}_5-\text{O}-\text{N}^5\begin{array}{c} \text{O} \\ // \\ \text{O} \end{array}$	189.2	$\text{C}_2\text{H}_5-\text{O}-\text{N}=\text{O}$ $\text{O}=\text{N}=\text{O}$
41. o-Chloronitrobenzene	299.9	301.7	$(\text{C}_6\text{H}_4\text{Cl})-\text{N}^5\begin{array}{c} \text{O} \\ // \\ \text{O} \end{array}$	301.3	$(\text{C}_6\text{H}_4\text{Cl})-\text{N}=\text{O}$ $\text{O}=\text{N}=\text{O}$
42. m-Chloronitrobenzene	298.9	301.7		301.3	
43. p-Chloronitrobenzene	300.0	301.7		301.3	
44. Azoxybenzene	444.7	447.8	$(\text{C}_6\text{H}_5)-\text{N}^5=\text{O}$ $(\text{C}_6\text{H}_5)-\text{N}^3$	446.6	$(\text{C}_6\text{H}_5)-\text{N}=\text{O}$ $(\text{C}_6\text{H}_5)-\text{N}$
45. o-Azoxy toluene	528.6	525.8	$(\text{C}_7\text{H}_7)-\text{N}^5=\text{O}$ $(\text{C}_7\text{H}_7)-\text{N}^3$	524.6	$(\text{C}_7\text{H}_7)-\text{N}=\text{O}$ $(\text{C}_7\text{H}_7)-\text{N}$
46. Benzantialdoxime N-methyl	325.9	329.3	$\text{Ph}-\text{C}-\text{H}$ $\text{Me}-\text{N}^5=\text{O}$	321.1	$\text{Ph}-\text{C}-\text{H}$ $\text{Me}-\text{N}=\text{O}$
47. *Nitric acid— from to	104.4 105.7	106.3	$\text{H}-\text{O}-\text{N}^5\begin{array}{c} \text{O} \\ // \\ \text{O} \end{array}$	105.4	$\text{H}-\text{O}-\text{N}=\text{O}$ $\text{O}=\text{N}=\text{O}$
48. p-Toluy lazide	307.0	306.3	$(\text{C}_7\text{H}_7)-\text{N}^3=\text{N}^5\equiv\text{N}^3$	336.3	$(\text{C}_7\text{H}_7)-\text{N}=\text{N}\equiv\text{N}$, or
				306.4	$(\text{C}_7\text{H}_7)-\text{N}\begin{array}{c} \text{N} \\ // \\ \text{N} \end{array}$
49. o-Toluy lazide	303.8	306.3	$(\text{C}_7\text{H}_7)-\text{N}^3=\text{N}^5\equiv\text{N}^3$	336.3	$\text{R}-\text{N}=\text{N}\equiv\text{N}$, or
				306.4	$\text{R}-\text{N}\begin{array}{c} \text{N} \\ // \\ \text{N} \end{array}$

TABLE II.—Continued.

Substance	[P] ob- served	[P] calcu- lated	New calculation	[P] calcu- lated	Calculation after Sugden
			Formula used		Formula used
50. Ethyl azido acetate	277.0	273.1	$\text{Et}-\text{O}-\text{C}=\text{O}$	306.2	straight N_3 chain, or
			$\text{CH}_2-\text{N}^{\oplus}=\text{N}^{\ominus}=\text{N}^{\oplus}$	276.1	N_3 -ring
			$\text{O}=\text{C}-\text{CH}_3$	250.4	straight N_3 chain, or
51. Azido acetate	220.9	213.6	$\text{O}=\text{C}-\text{CH}_2-\text{N}^{\oplus}=\text{N}^{\ominus}=\text{N}^{\oplus}$	220.3	N_3 -ring

maintain a constant value of the multiple bond but according to the precedent of atomic refractivities different values have been calculated for $-\text{O}-$ and $\text{O}=\text{O}$, $-\text{S}-$ and $\text{S}=\text{S}$, $-\text{Se}-$ and $\text{Se}=\text{Se}$, $-\text{Te}-$ and $\text{Te}=\text{Te}$, as well as for $-\text{N}<$, $-\text{N}=\text{N}$, and $\text{N}\equiv\text{N}$. Indeed, the many different values needed for molecular refractivities of nitrogen or sulphur compounds would suggest that the double-bond values themselves also would be affected by the state of valency of atoms, being different, e.g., in the nitro and the nitroso group. But additivity is already obtained if the $>\text{C}=\text{O}$ and $-\text{C}\equiv\text{N}$ values are taken, as long as these atoms are concerned, and the respective multiple bond values for the *negative* atom in all other cases. This simple rule established one parachor value only for all atoms in higher states of valency, as they invariably act as the positive end of a dipole moment. All numerical values will be found in Table I.

Finally, all increments for the formation of rings can be taken over from Sugden's calculation and Mumford and Phillips' ⁶ value for hydrogen in the hydroxyl group, where it is about one-third lower. This is entirely analogous to conditions prevailing for molecular refractivities. It is the only case where a change of polarity makes itself perceptibly felt in parachor calculation, while similar conditions are often met with in molecular polarizabilities. On the other hand, the latter does not need special purely geometrical factors, e.g., for the formation of rings. Refractivities measure the polarizability of the electron cloud and the parachor is essentially a measurement of volume.

⁶ S. A. Mumford and J. W. C. Phillips, J. Chem. Soc., p. 2112 (1929).

It is therefore not surprising that the former is more affected by factors of polarity, the latter more sensitive to geometrical influences.

The calculations of atomic parachors are now carried out in Table I. For molecular refractivity it has become customary not to use values from literature, but to measure refractive index and density of the same specimen. Sufficient measurements of this kind are not available for the parachor in all cases. We have therefore preferred to base the fundamental values on such molecules, which are simple in structure, easier to be purified in the liquid state, and do not possess an enhanced polarity which in some degree might lead to an ionic dissociation.

3. ATOMIC PARACHORS AND MOLECULAR STRUCTURES

In Table II, observed molecular parachors of a number of typical molecules⁷ are compared with those calculated in accordance with Sugden's method as well as the constants derived in Table I. Table II therefore provides justification for this subdivision into atomic parachors according to the state of valency, and also for the structural formulae in which no use is made of semipolar or singlet linkages or their counterpart of resonance structures. A still better agreement between calculated and observed parachors could be reached by taking for the atomic parachors the mean values from measurements of a number of similar molecules instead of one value only from one particular molecule and measurement.

⁷ Besides the experimental values collected by Sugden, reference 1, those of D. L. Hammick, R. C. A. New, N. V. Sidgwick, and L. E. Sutton, J. Chem. Soc., p. 1876 (1930) have been used for the isocyanides.

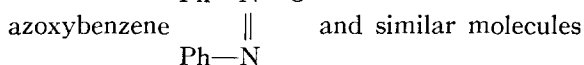
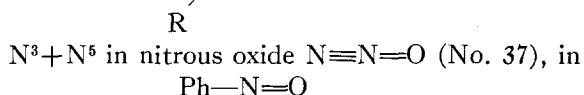
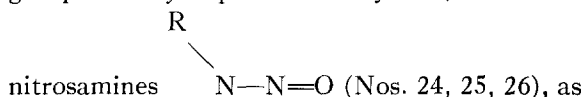
The constants of Table I are still unnecessarily afflicted by fortuitous experimental errors. However, this method of comparison suggested itself as better suited for the present purpose which is to demonstrate that the division of molecular parachors into atomic constants according to the state of valency rather than according to different kinds of covalent linkage, is entirely workable.

It will be seen that the newly calculated values are as good as the old ones, and in general there is little to choose between them. All through the old structural formulae have been used. Indeed, it is very gratifying to observe the almost automatic working of these formulae. To mention

TABLE III. Atomic parachors and periodic table.

H	17.1				
He	20.5				
Be	(22.8)				
B	15.9				
>C<	4.8	Si ⁴ 28.7	Ge ⁴ 40.1	Sn ⁴ 57.9	Pb ⁴ 75.0
C ²	28.0			Sn ² (75)	Pb ² (86)
N ⁵	1.7	P ⁵ 18.3		Sb ⁵ (40)	
N ³	17.4	P ³ 37.1	As ³ 50.3	Sb ³ 66.0	Bi ³ (~80)
		S ⁶ 13.9			
		S ⁴ 29.5	Se ⁴ 45.2	Te ⁴ 58.7	
O<	20.5	S ² 49.8	Se ² 65.6	Te ² 77.4	
F	(25)	Cl 54.3	Br 68.0	I 91.0	
Ne	25	Ar 54			

just one instance. The parachor value of a N₂ group is fully represented* by N³+N³ in the



(Nos. 44, 45), while the azide group —N=N≡N obtains its value from 2N³ + 1N⁵ (Nos. 48 to 51). Hence we are now in a position definitely to state, firstly, that if they should exist, *the parachor is unable to distinguish* between different varieties of covalent linkage, and, secondly, that these classical structures which recognize only

* Superscripts mark the state of valency, not the charge.

one kind of covalent bond, *are entirely sufficient for the representation of such additive molecular constants* as the parachor or molecular refractivities.

Attention may now be drawn to some details of Table II, and first of all to those molecules the parachor of which has not been explained before. These simple molecules with "anomalous" parachor are listed by Sugden¹ as N₂, O₂, N₂O, CO, CO₂, SO₂, and SO₃. We have not been able to calculate [P](SO₃) satisfactorily, and as it is the only one which is left, the experimental value might not be entirely reliable. Most of the other molecules are already included in Tables I and II. (Cf. Table I, Nos. 2, 3, 16; Table II, Nos. 1 and 37.) Thus CO has been used to calculate [P](C²), and the same value of C² has been checked by the calculation of the isocyanides. From CO₂ we took the value of O=, verified by numerous other molecules containing a double bonded O atom. The N₂ molecule was used to calculate the value of the triple bond between N and N, and the same value for N≡ then occurs again in the azide group —N=N≡N. Finally, [P](N₂O)=81.1 (obs.) can be calculated according to N³+N⁵+O or 43.0+1.7+36.4=81.1. The parachor for oxygen, O₂, has been observed as 54.0. This value is fully represented by adding the parachors of two O atoms plus one oxygen-double bond, or [P](—O—)+[P](O=)=20.5+36.4=56.9.

The disappearance of anomalous parachors to our mind presents intrinsic evidence for this method of subdivision approaching nearer to reality.

Another type of molecule, where the present method has a decided advantage over the old one, is that formed by the azide group. The two methods give these values of the parachor of the possible configurations

I	II
[P] (Sugden) 77.4	107.3,
[P] (pres. method): 84.6	77.3;
observed: [P] N ₃ =77.2.	

The observed mean value [P](N₃) of 5 azoimides is 77.2. Consequently, Sugden had to

ascribe the ring structure to the azide group, while the open chain would be preferred for the present calculation. In the meantime electron diffraction measurements⁸ have shown that methyl azide possesses the open chain structure (with a valency angle $\text{CNN} = 120^\circ$). Even on the basis of the resonance interpretation of coordinate bonds there is hardly a possibility open to change this result, because the observed dipole moment and interatomic distances agree too well with those calculated on the basis of the classical formula II. This will be shown in Part II (Section 3) of this paper.

4. ATOMIC PARACHOR AND ATOMIC NUMBER

In Table III and in Fig. 1 the parachors of atoms are collected according to their position in the periodic table.*

The following conclusions suggest themselves immediately:

(1) In a column of the periodic table, i.e., proceeding from C to Pb, N to Bi, O to Te, and F to I, the atomic parachors increase regularly with the main quantum number, as they ought to do if the parachor measures the atomic volume in covalent linkage. This is also true for different states of valency.

(2) The atomic volume of the same atom in a lower state of valency is always larger than in a higher state. Indeed, the transition from C^2 to C^4 , N^3 to N^5 , etc., always implies the activation of two more electrons (in most cases the outside s^2 electrons, but a $\pi(p)$ pair in such atoms as S^4). While on an atomic orbital in the lower state,

they are changed to a molecular orbital in the higher one. Here they partly belong to the other atom, and while increasing the volume of the latter, they decrease that of the former. It will be seen that the lowest parachors are with those atoms like N^5 which can only be the positive partner of any combination, the largest with those like S^2 or Cl^1 which most frequently form the negative partner.* In other words, the volume taken up by a particular atom in a covalent molecule largely depends on the shift of the electrons from it or towards it. This appears to agree well with the calculation of Lennard-Jones and Corner,⁹ in which the molecular parachor is a function of the attractive and repulsive intermolecular potentials.

(3) A multiple bond always increases the atomic parachor. For the parachor as a function of the molecular volume this is by no means an obvious result because the covalent radii¹⁰ are shortened by the multiple bond. As electron diffraction and x-rays in the main measure the position of the nuclei, and as also the atomic refractions are increased by multiple bonds, the increase of volume has again to be attributed to the binding electrons. This effect, which could be pictured as a kind of spreading of the electrons in space, is of course connected with directions of the bonding orbitals.

(4) In comparing the atomic parachors in the same period, i.e., from Be to F and Ne, etc., the change of atomic volume appears to be regulated by the ionization potential. The following points suggest themselves: (a) In the series Be^2 , B^3 , C^4 , N^5 , and similarly for Si^4 , P^5 , S^6 , in which all the valence electrons are chemically active, the atomic volume steadily becomes contracted with increasing nuclear charge. (b) The same is true for C^2 and N^3 , P^3 , and S^4 , or the series Sn^2 , Sb^3 , Te^4 , for which the nucleus is always screened by the same number of electrons (in these atoms the two outside s electrons). (c) Conditions are different for a series of atoms like C^4 , N^3 , O^2 , F^1 , Ne, or Si^4 , P^3 , S^2 , Cl^1 , and Ar. Here the nuclear

⁸ L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 13 (1937).

* Some of them are not yet certain. Those of Sn^2 , Pb^2 , and Sb^5 cannot be checked for lack of experimental data, and the chlorides from which they are calculated are near to the limit of electrovalent linkage. Some fraction might already be dissociated into ions according to the varying experimental conditions. Those for some metals, particularly Be, have to be taken from chelated compounds in which the organic radicals form rings [cf. N. V. Sidgwick, *The Electronic Theory of Valency* (The Clarendon Press, Oxford, 1927)]. To our mind, this is due only to enhanced dipole forces between Be and the double-bonded oxygen atom (cf. references 2 and 4). It is therefore difficult to decide whether this ring has to be recognized as a co-volume and an increment for ring formation is to be included in the calculation. In that case the atomic parachor of Be from its acetyl acetate comes to 10.6, without the ring constant to 22.8. The latter figure has been tentatively adopted, mainly because the covalent radii [see L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1939), p. 154] decrease as $\text{Be} > \text{B} > \text{C} > \text{N}$.

* This point is brought out still more clearly in the system of atomic refractivities, where it is easy to distinguish between, say, P in PH_3 and in PCl_3 . The numerical values are $\text{P}^{3-} = 8.54 > \text{P}^{3+} = 6.55$ (cf. reference 12).

⁹ J. E. Lennard-Jones and J. Corner, Trans. Faraday Soc. **36**, 1156 (1940).

¹⁰ Cf. L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1939), p. 154.

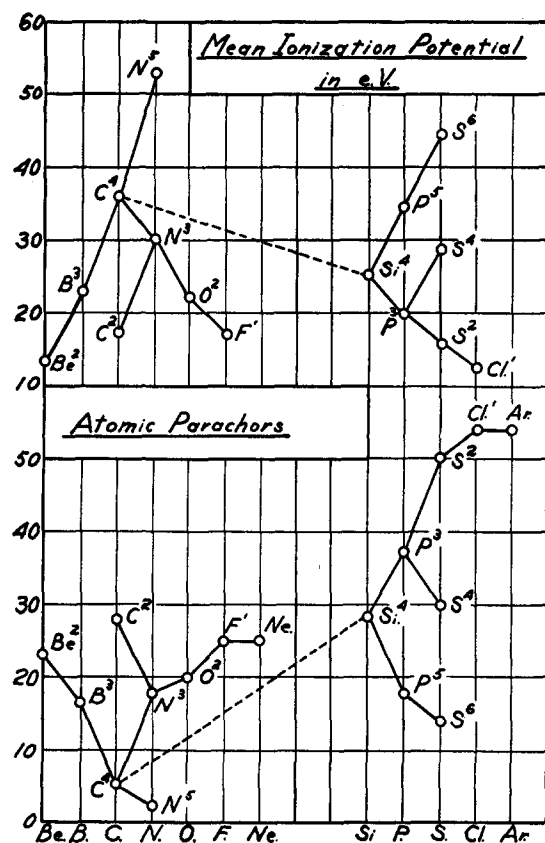


FIG. 1. Covalent parachors and mean ionization potentials of atoms.

charge and the number of electrons increase step by step, but less and less take part in the chemical bond. Hence the volume contributed to that

of the covalent molecule by the reference atom increases more and more, obviously converging to the numerical value of the free rare gas atom, which follows.

This behavior suggests the strength of the nuclear field as the main factor on which the parachor depends, and in order to test this concept the mean ionization potential per valence has been added in Fig. 1. This quantity has been introduced earlier¹¹ as a convenient means to follow the transition from covalent to electrovalent linkage. It is the arithmetic mean for all the ionization potentials relevant to the particular state of valency, e.g., the mean of the first, second, and third ionization potential of N for N³, that of the first to fifth for N⁵.

As will be seen at once, the two curves of atomic parachors and mean ionization potential have the general character of mirror images. In other words, the higher the mean ionization potential, the more the electron cloud is contracted and hence the smaller the volume contributed by the particular atom to that of a covalent molecule.

Finally, a comparison of the atomic parachors with atomic refractivities suggests itself. The latter ones are understood to be the contributions of the individual atoms to the polarizabilities of covalent molecules. Attempts have been made to

¹¹ R. Samuel and L. Lorenz, *Zeits. f. Physik* **59**, 53 (1929); R. F. Hunter and R. Samuel, *Chem. and Ind.* **55**, 733 (1936).

TABLE IV. Atomic refractivities in covalent inorganic molecules (for D lines). (Superscripts indicate the state of valency in polar covalent linkages, but not ionic charges.)

H 1.04 (H ⁺ 0.98)				
He 0.50				
B 3.51				
>C< 2.42	>Si< 4.87	>Ge< 8.34	>Sn< 11.24	>Pb< 13
C ² 2.93				
N ²⁺ 2.52	P ⁵⁺ 6.55			
N ³⁺ 3.90	P ³⁺ 8.54			
>N ³⁺ — 2.3, ≡ N ⁵⁺ 3.07	P ³⁻ 8.65			
	S ⁶⁺ 2.99	Se ⁶⁺ 4.66	Te ⁶⁺ 6.10	
	S ⁴⁺ 6.19	Se ⁴⁺ 11.1		
—O— 1.64, O=2.21	S ²⁺ 7.5, S ²⁻ 8.31			
—O' 4.06				
(O''~7)				
F ⁻ 1.45	Cl ⁷⁺ 2.63	Br ⁻ 8.72	I ⁻ 16.02	
Ne 1.00	Cl ⁻ 5.82			
	Ar 4.20			

establish additive values of refractivities for inorganic molecules which would reduce the great number of empirical constants used for calculations of molecular refractivities, but none has entirely succeeded for a number of reasons. These are partly of theoretical, partly of experimental nature. For instance, even disregarding variations of polarity, the average value of the polarizability α should be split according to the various axes of the molecule and α extrapolated to infinite wave-length, in order to obtain strict additivity. At the same time, all such molecules would have to be discounted, for which the reference wave-length of measurement is too near to their first absorption band and already for such simple

TABLE V. Molecular refractivities (*D* lines).

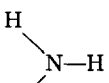
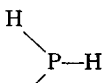
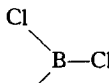
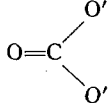
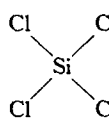
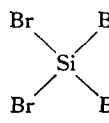
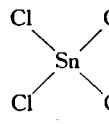
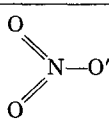
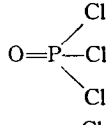
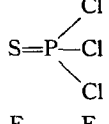
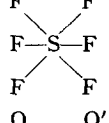
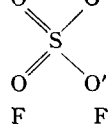
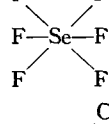
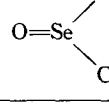
Molecule	Formula used	Mol. refractivity calc.	Mol. refractivity obs.
HCl	H—Cl	6.86	6.67
H ₂ O	H—O—H	3.72	3.76
NH ₃		5.33	5.61
PH ₃		11.72	11.68
BCl ₃		20.97	20.97
CO ₂	O=C=O	6.84	6.68
[CO ₂]"		12.18	12.27
CS ₂	S=C=S	22.50	22.13
SiCl ₄		28.15	28.15
SiBr ₄		39.65	40.85
SnCl ₄		34.52	34.52

TABLE V.—Continued.

Molecule	Formula used	Mol. refractivity calc.	Mol. refractivity obs.
[NO ₂]'		11.00	11.00
N ₂ O	N≡N=O	7.80	7.31
POCl ₃		26.22	25.13
PSCl ₃		32.8	32.65
SF ₆		11.67	11.69
[SO ₄]"		14.39	14.63
SeF ₆		13.36	13.36
SeOCl ₂		25.0	25.0

molecules as Cl₂, HBr, CS₂ this condition hardly holds.

However, even without strict additivity, reasonable constant values of atomic polarizabilities may be calculated, and it is of some theoretical interest to show the existence of a near relationship with the atomic parachors, although the two constants are obtained in such entirely different ways. For the sake of convenience only, a set of figures published earlier¹²

¹² R. Samuel, Zeits. f. Physik 49, 95 (1928). The value for the contribution of oxygen with one covalent and one electrovalent link to a molecule such as [NO₂]⁻ has been derived under certain assumptions which would not be made today. They are not necessary, as this value could be taken directly, e.g., by comparing CO₂ and [CO₃]²⁻. The refractivities of PSCl₃ and SeOCl₂ have been added and that of POCl₃ has been changed according to the paper of C. P. Smyth, G. L. Lewis, A. J. Grossman, and F. B. Jennings, J. Am. Chem. Soc. 62, 1219 (1940). The symbol R (X) is used to indicate the molecular or atomic refractivity of the molecule or atom X.

is used here (Table IV) and comparison of calculated and observed data (Table V) shows, that they are sufficiently accurate and additive to indicate the relation of atomic polarizibilities and atomic number in simple covalent inorganic molecules.

It will be seen (1) that different values obtain for different states of valency, e.g., $R(S^6) = 2.99$, $R(S^4) = 6.19$. That of the higher one is always smaller, i.e., the chemically inactive electrons follow more easily the outside field.

(2) Separate values for the same atom in the same valence state are necessary, according to its being the positive or the negative partner of the combination. Obviously the polarizibility is more sensitive to polarity of the bond than the parachor, where such a condition prevailed only for hydrogen in the $-OH$ group.

(3) The multiple bond always increases the polarizibility.

(4) The polarizibility of atoms in covalent linkage increases in a column of the periodic table, e.g., from F to Cl or C to Pb exactly as the parachor (and also as Fajans' refractivities of free ions).

(5) The polarizibility of an atom in covalent linkage is larger than that of its positive and smaller than that of its negative ion; the former possesses less electrons than the atoms and these are held in a field of excessive positive charge, while the latter possesses more electrons than the atom, in excess of its nuclear charge. This is clearly shown by the three values of oxygen. The first $R(-O-)$ is that in organic molecules $R-O-R$, the second $R(-O')$ that contributed by one of them in an anion such as $[NO_3]'$, the third¹³ that of the free ion O'' . The parachors of positive and negative ions have been discussed by Mumford and Phillips⁶ who in general find quite similar conditions.

(6) In a period, the atomic refractivities follow in general the reciprocal value of the (mean) ionization potential, as was to be expected.

The comparison of atomic parachors and atomic refractivities shows that both are similar in some respects, but vary in others. Thus stereometrical factors play a role in parachor calculations, to wit, the special increments for ring

formation. Nothing similar is known for molecular refractivities. On the other hand, these are influenced so much more by the polarity of the bond that different values have to be introduced for the same atom as the positive or negative end of a dipole. Furthermore, the well-known "exaltations" of molecular refractivities in conjugated double bonds and similar structures indicate that the polarizibility is affected by the non-localization of the electrons, itself theoretically connected with the polarity of the molecules. This influence is sufficiently great to consider these exaltations as a measure of the mobility of these electrons, but no similar effect obtains for parachor values.

Apparently both depend, as stated above, on stereometrical as well as on polarity factors, but in different degrees. Refractivity, an induced dipole moment in the first instance, cannot be but affected by stereometrical arrangements within the molecule, e.g., a change in the length of the bond. The parachor is essentially a measurement of atomic volume, but, as said before, this itself depends on the cloud of electrons and their polarization therefore will have repercussions on the volume.

In order to estimate roughly the influence of these two kinds of factors on our two constants, they might be compared with other quantities known to represent one of these classes in particular. The length of the bond on the one side and the ionization potential on the other suggest themselves for such a purpose. However, as they run roughly anti-parallel in the periodic table, the one increasing from period to period, the other decreasing in the same sense, there is only one possibility left. On account of the difference in electronic structure in the preceding elements Ni, Pd, and Pt, the ionization potential runs irregular for the following atoms, e.g., for Cd it is lower than that of *both* its neighbors Zn and Hg. The covalent radius is hardly affected and the ionic radius not at all. Hence, in Fig. 2 atomic parachors and refractivities are compared with these constants. It will be seen that the depression of the mean ionization potential of Cd is reproduced in the enhanced polarizibility of Cd, as well for the free atom in the metallic vapor, as also for the atom in the covalent linkage of the diethyls. For the parachors, only values

¹³ K. Fajans and G. Joos, *Zeits. f. Physik* **23**, 1 (1924).

for the free atom in the fused metallic state are available. Although not as entirely unaffected as the ionic radius, the curve follows much more closely that of the covalent radius than that of the ionization potential or the refractivities of the free atoms.

5. CONCLUSIONS

It has been shown that a system of additive atomic constants can be set up for the molecular volume, measured by Sugden's parachor, which is based on the classical structural formulae of chemistry. It is characterized by different constants for the same atom in different valence states, but does not resort to different constants for different types of covalent linkage.

It could be argued that any better agreement between observed and calculated values in this new representation is simply due to the greater number of independent constants. But in the older representation a number of molecules (anomalous parachors) could not be accounted for. They could find their place in the additive system only through the introduction of special constants, one for each molecule. As the present procedure takes care of these molecules automatically, the total number of additive constants has not really been increased.*

* For any additive molecular constant there remains indeed a third possibility of subdivision into additive contributions. Molecular refractivities, for instance, instead of being separated into atomic refractivities, also have been divided into bond refractivities. Rather than considering the contributions made to the polarization of a molecule by the electrons belonging to a particular atom, those of the electrons (of different atoms but) together forming a particular bond are examined. [A. L. V. Steiger, *Ber.* **54**, 1381 (1921); K. Fajans and C. A. Knorr, *Chem. Zeits.* **48**, 403 (1924); C. P. Smyth, *Phil. Mag.* **50**, 361 (1925); K. G. Denbigh, *Trans. Faraday Soc.* **36**, 936 (1940)]. As the dipole moments on account of their vector character have to be separated not into atom or group contributions but into bond moments, a comparison of the polarizabilities per bond has a good physical meaning. A distribution of the molecular parachors into bond parachors, however, appears not to serve a useful purpose and we have refrained

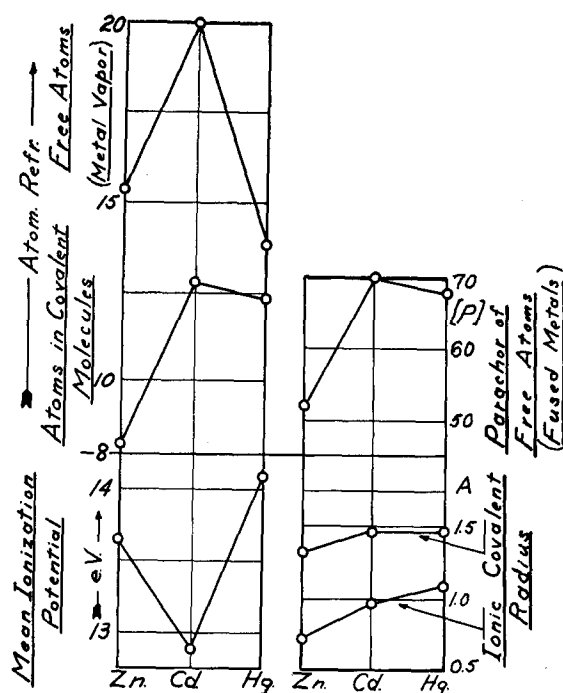


FIG. 2. Comparison of electrical and stereometrical factors.

On the other hand, the present system is superior to the older one in its correct representation of some molecules, e.g., the azides, and, most important of all, in conjunction with dipole moments, the new measurements of the bond distances have ruled out the application of constants for a coordinate link of all such standard molecules as SO_2 , SOCl_2 , POCl_3 , etc. Hence there appears no other alternative left but to accept the present set of atomic constants.

The fact that such a separation of molecular into atomic parachors on the basis of the classical formulae is at all possible, makes it evident that the parachor is unable to distinguish between different equivalent structures or theories.

from doing so. The number of constants to be used to achieve perfect additivity quite obviously is always the same, whatever method of subdivision is used.