

# A PRAGMATIC SYSTEM OF NOTATION FOR ELECTRONIC VALENCE CONCEPTIONS IN CHEMICAL FORMULAS

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This paper presents for consideration some questions and points of view bearing upon the methods of indicating within chemical formulas electronic conceptions of valence now in vogue.

Alfred W. Stewart (1) in his latest volume, "Recent Advances in Organic Chemistry," states that "The greatest problem before Organic Chemists at the present day is the application of modern electronic views to the salient phenomena among the reactions of carbon compounds." If we accept this dictum, we are immediately confronted with two pertinent questions. First, in what manner and to what extent should the chemist's graphic or structural formulas be modified so as to conform rationally with current notions of electronic valency? Second, will such modifications elucidate or will they confuse the fundamental purpose of a structural formula, which, as all chemists agree, should not only present a picture of the number, the kind, and the arrangement of the atoms within the chemical molecule but also clearly indicate and correlate the manifold chemical reactions displayed by the molecule.

The import of both of these perplexing questions has been fully sensed and expressed by John A. Cranston (2) in the opening paragraph of an address entitled "Symbols for Electronic Bonds" in these words:

The development of the electronic theory of valency has not been accompanied by an expansion in symbolism adequate to express without ambiguity the large number of ideas that exist concerning the bonds that unite atoms together in a molecule. The horizontal line which originally indicated a chemical bond, the dot, and the plus and minus

signs [and let me add the complicated cubical octet notations imposed upon structural formulas by some enthusiasts] have borne too big a burden in the development of the theory of valency and none of them are now free from ambiguity.

Cranston then proceeds to show that the theories of Lewis (3), Fry (4), Lowry (5), Noyes (6) Sugden, Kermack, and Robinson (7) are collectively devoid of any uniformity in symbolism and that in many instances the symbolism employed is open to various contradictory interpretations which naturally provoke confusion. To obviate these difficulties, Cranston recommends a symbolic notation, based on an idea of Main Smith (8), namely that "The symbol is a line, which indicates a shared electron, terminated by a dot placed at the end nearer to the atom to which the electron belonged before combination. An isolated dot represents an unshared electron."

A critical examination of Cranston's system of electronic valence notation which is designed to illustrate non-polar single bond or doublet or co-valent bond, semipolar single, semipolar double, non-polar double, and non-polar triplet linkages, will likely lead many to conclude that it may also, *per se*, be open to many of the objections which he wages against current systems of notation.

It should here be noted that no theory in any science has been so marvelously fruitful as the structure theory of organic chemistry. It has enabled chemists to predict the discovery and properties, both physical and chemical, and to effect the synthesis, both in the laboratories and in the industries, of thousands of compounds of inestimable value to mankind. And now when we are considering methods of modifying this structure theory of organic chemistry, by imposing upon its structural formulas an electronic valence symbolism, are we not, as practical chemists, obligated to see to it that such system be one that is calculated to elucidate our formulas rather than render them obscure through the application of metaphysically involved implications on atomic structure which are extraneous to the real chemical significance of the structural formulas *per se*. In other words, the opinion is now growing that the structural formula of the organic chemist is not

the canvas on which the cubist artist should impose his drawings which he alone can interpret. Indeed, many chemists, some of whom will be quoted later, believe that the employment of a simple plus and minus polar valence notation is all that is necessary, at the present stage of our knowledge, to effect the further elucidation of structural formulas. On the grounds that practical results are the sole test of truth, such a simple system of electronic valence notation may be termed "pragmatic."

An inquiry into the reasons, historical and perhaps psychological, why many chemists are inclined to impose upon structural formulas an octet system of valence notation may not be out of place.

In 1863-1864, Newlands first drew attention to the fact that when the elements then known were placed in the order of their ascending atomic weights, each element was found to resemble the eighth beyond or before it in the list. This remarkable relation was called the Law of Octaves and upon it Mendelejeff, in 1869, constructed the Periodic System which, apart from its prediction of new elements, served as a most valuable means of enabling chemists to differentiate between the atomic and equivalent weights of elements. When these fundamental distinctions were effected, the valence of an element could be accurately, empirically, and pragmatically defined as the number of its equivalent weights contained within its atomic weight. If an element displays multiple valences, it is because it has more than one equivalent weight and not necessarily because it can gain or lose electrons or share pairs of electrons in the production of polar or non-polar valences. Practically all chemists are agreed that atoms may gain, lose, and share electrons but does anyone know just how they do it and how it is all to be indicated in the graphic formulas of atoms and molecules? For the elucidation of our human confusion, Lewis and Langmuir, on the one hand, and Rutherford and Bohr on the other, with their respective physical, physico-chemical, and chemical disciples, have presented pictorial hypotheses which are not as yet quite reconcilable.

While these admirable alternate hypotheses are advocated by many, most chemists, I believe, are more partial to the Lewis-

Langmuir conception of electronic shells than to the Bohr conception of electronic orbits. A possible reason for this attitude may be the fact that the cubical octet conception is primarily and fundamentally an outgrowth and a pictorial elaboration, in terms of atomic structure, of the original conception of Abegg and Bodlander (9), who, in 1899, stated that atoms display different kinds of valency termed "normal" and "counter" valency of opposite polarity according as they are united with electropositive and electronegative atoms. Furthermore, it is a question in the minds of many chemists whether or not the Lewis-Langmuir valence conceptions and notations possess any more, or perhaps as much, truly chemical significance as that which characterizes the Abegg and Bodlander system.

Now when we come to consider the actual chemical properties of atoms and molecules, no matter what attempts may be made to explain valency by an electronic pictorial notation, all that the chemist knows pragmatically about the valence of an atom may be embodied in the simple fact that if ( $n$ ) be the empirically determined valence of a given atom, that atom may function in ( $n + 1$ ) different ways. This has been fully illustrated in the numerous publications (10) of the interpretations of a great variety of chemical reactions. This is also a direct and simplified modification of the conceptions of Abegg and Bodlander and it does not require the amplification and entailed ambiguity necessarily encountered when the cubical octet or other systems of electronic valence notation are imposed upon structural formulas. It enables us to correlate in a simple fashion the several ways in which atoms and radicals react, positively, negatively, and amphotericly, in strict conformity with the actual chemical behavior of the molecule as amply illustrated by the well established chemical reactions actually being dealt with such as ionization and electrolysis, hydrolysis, and oxidation-reduction processes. In fact, practically all chemical phenomena may be classified under these types.

This idea and procedure may be termed "chemical pragmatism." It takes issue with attempts to embody within the structural formulas of the chemist's molecule the diverse meta-

physical hypotheses which are concerned chiefly with questions relative to the constitution of the atom and the disposition of its valence electrons. Of course, the more chemists know about the constitution of the atom, the more fully can they explain the chemical properties of the atom *per se*, but we must not lose sight of a paramount philosophical truth, developed by Immanuel Kant in his Critique of Pure Reason, namely the antinomies of pure reason which warn us that whenever assumptions or hypotheses are based upon premises that lie beyond the territory of sensation experience, that is, can not be observed or demonstrated through tangible experimentation, absolutely contradictory conclusions are bound to follow.

That this state of affairs is all too prevalent is attested by the previously noted plea of Cranston (2) for the adoption of a rational system of electronic valence notation. Not only the readers of journals, but some editors sense it. For example, an editorial note published in the Journal of the Society of Chemical Industry states that

Discussion of alternate polarities and kindred topics is of great importance, and we hope the letters we have published in these columns have cleared away a considerable mass of misapprehensions. We are, however, obliged to wait for a period before dealing with the subject again; *a proportion of our readers fails to understand the whole of the arguments without a mental effort which is made unwillingly.* (Author's italics.)

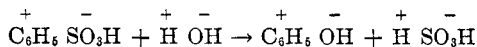
It is also evident that the authors of these arguments also frequently fail to comprehend one another. If you doubt this statement, just call to mind the arguments in an electronic valence discussion at any chemical society meeting. Two advocates of one and the same system of electronic valence notation will be diametrically opposed in their interpretation of the electronic character of a given atom or radical of a molecule: one says it is positive; the other claims it to be negative; and the chances are very strong that a third advocate of the same theory will arise and maintain that it is neither positive nor negative but non-polar because the electron pair is just midway in its location between

two atoms. Arguments on atomic structure then follow to show why the electron pair is more the property of one atom than of another and, in the end, all are wondering, both polar and non-polar advocates, "how many angels can dance on the point of a needle." Such disputes can be settled only by direct reference to the actual chemical behavior of the substance whose electronic formula is under discussion, and *only that formula should be assigned to the molecule which is in conformity with its particular behavior at that particular time.* As is well known, a given substance may be an electrolyte or polar compound in one solvent or it may be a non-electrolyte or a non-polar compound in another solvent. Temperature, concentration, and catalytic agents are other conditions which completely alter the character and reactivity of the molecule. *It is therefore impossible to state that a given substance is specifically a polar or a non-polar compound.*

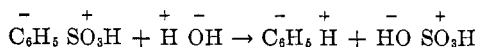
The electronic valence skeleton in the chemist's closet embodies many bones of contention, but its spinal column is the arbitrary distinction that has been set up between polar and non-polar compounds. W. A. Noyes (11) once stated that "The difference between polar and non-polar valencies is one of degree and not of kind." G. N. Lewis (12) has stated that "even a symmetrical molecule like that of  $H_2$  or  $I_2$  may from time to time become polarized in one direction or the other, as a consequence of the disturbance due to thermal motion. . . . In other molecules some displacement of electrons may occur without full ionization." Julius Stieglitz states that "Polarity exists wherever there is a difference in charge, positive and negative, between two atoms, and it is so valuable a conception in the treatment of organic compounds, non-electrolytes, that it must be clearly insisted upon. Again, just recently, Tanasescu (13) has emphasized the fact that chemists, notably those of the American school, influenced by data relative to the electronic conception of matter, that is of the constitution of the atom *per se*, have not considered the totality of the reactions of the organic molecule but rather have preferred to show with the greatest precision possible the nature of the affinities between atoms. Tanasescu deems it preferable to regard electronic conceptions of valence as independent of con-

ceptions relating to the inner nature of valency and maintains that, in the search for the specific mechanisms of atomic unions as complex as those of the organic molecule, *only a theory of polarity much more simplified will be of real interest and success.* All of this is dependent upon correlations which should be based primarily and fundamentally upon the actual chemical reactions of the organic molecule. Tanasescu further states that "even if the organic molecule is not capable of furnishing ions, as commonly conceived, we can always consider it as being susceptible to dissociation into atoms or radicals charged with quantities of electricity of equal and opposite sign."

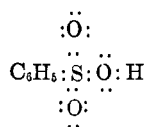
These points of view were originally advanced by Fry (4) in his various papers and monograph on the electronic conception of positive and negative valence and the constitution of benzene, and in his conceptions of *electromers* and *electronic tautomerism*, which afforded an explanation of the Crum Brown-Gibson benzene substitution rule and the *simultaneous* formation of ortho, meta, and para substituted derivatives of benzene (14). A given derivative of benzene, for instance phenylsulfonic acid (15)  $C_6H_5SO_3H$ , may react either as the electromer  $C_6H_5SO_3^+H^-$  or the electromer  $C_6H_5^+SO_3^-H$ . The particular reaction occurring depends wholly upon the specific experimental conditions under which the reaction takes place. Thus, for instance, hydrolysis of phenylsulfonic acid *in alkaline solution* yields phenol and sulfurous acid while in *acid solution*, the products are benzene and sulfuric acid. Entirely apart from the question of whether phenylsulfonic acid is a polar or a non-polar compound, it reacts in the former case in strict conformity with the simple pragmatic polar valence formulas notation



and in the latter case as



Furthermore, there is nothing whatever in the shared electron octet polar valence system of notation for phenylsulfonic acid which Lewis (16) represents by the cumbersome formula



to indicate or to correlate directly its actual chemical behavior with its electronic structure, much of which is quite extraneous to the specific reactions in question. Lewis virtually begs this question in the following words:

It is no longer necessary to consider this substance as a mixture of two tautomeric forms [electromers], in one of which the phenyl group has a unit positive charge, and in the other of which it has a unit negative charge. . . . We see that the bonding pair between phenyl and sulfur may be shifted toward the one or the other, and when the molecule is broken at this point, the phenyl group, if it retains possession of the bonding pair, will combine with hydrogen ion but if it loses possession of the bonding pair will combine with hydroxyl ion.

Furthermore, this statement of Lewis may be regarded as a direct admission that phenylsulfonic acid does react under the different conditions noted as *two distinct tautomeric forms*, for if, in one case, the electron pair is in one position in the molecule and if, in the other case, the electron pair occupies a different position in the molecule, he is then undeniably dealing with two distinct electronic formulas, electromers, which are most simply and pragmatically represented by the polar valence formulas  $\text{C}_6\text{H}_5^+\text{SO}_3^-\text{H}$  and  $\text{C}_6\text{H}_5^-\text{SO}_3^+\text{H}$ . In substance, Lewis attempted to paint a shared electron picture in one structure of two distinct tautomeric forms which Fry (17) earlier defined as the electromers or the electronic tautomers of phenylsulfonic acid. This is cited as only one of many illustrations wherein the simple pragmatically employed polar valence formula notation has been sacri-



ficed for the more complicated and abstruse shared electron and octet notation.<sup>1</sup>

Some critical students have asked if this is not partly due to a current fashion or the common custom of courting popularity by adopting the latest ideas. I am reminded, in this connection, of a bit of advice received from a well known former advocate of the simpler electronic polar valence notation who urged me to drop the plus and minus notations and, as he expressed it, "get on the Lewis-Langmuir band wagon." Pragmatic chemists are not naturally disposed to discard the violin for the saxophone, even though both instruments may be profaned. Moreover, pragmatic chemists are not going to subscribe to a theory because it is fashionable or because of the psychological truth that "if you repeat something often enough, loudly enough, and blandly enough, eighty per cent of the world will believe it," regardless of its intrinsic merits or demerits.

All of this brings us back again to that dry bone of contention, namely the distinction between polar and non-polar compounds. The necessity for such a distinction does not concern pragmatic chemists, several of whom have been quoted in this paper. Further, in this same connection, James Kendall (18) has recently written two very significant statements in his admirable textbook on Inorganic Chemistry. First, "it is immaterial to us at this stage whether the Lewis-Langmuir conception of electron shells or the Bohr conception of electron orbits is finally accepted." Second, "Strictly speaking, the distinction between polar and non-polar substances is not fundamental but one of degree only." In the same vein, Professor K. George Falk, (19) one of the original advocates of the simpler electronic polarity formulas, writes "While it must be admitted that the octet theory is interesting to study, fascinating to work with, and permits of ready popular

<sup>1</sup> For more recent direct experimental evidence for the existence of electromers, "Two Forms of Ortho-Nitro-Toluene," see Clark and Crozier, Transactions of the Royal Society of Canada, 3rd series, Vol. XIX, 157 (1925). See also the survey by Clark and Carter, *ibid.*, Vol. XXI, 323 (1927), on "The Replaceability of Nitro Groups from the Nucleus of Various Aromatic Compounds," one hundred and ten in number.

presentation, at the same time the question may well be asked whether this theory as such adds anything real to an understanding of chemical reactions." While "the use of shared electrons for explaining chemical reactions possesses apparent advantages in some cases it would seem as if more definite postulates as to the positions of the shared electrons should be available before the formulation will possess real significance. *It may therefore be questioned whether the octet theory or the shared electron theory at the present time contributes any essential relation to the simple electron transfer valence view;*" that is, to the plain polarity valence formula notation. (Author's italics.)

Julius Stieglitz also strongly advocates the employment of a pragmatic system of electronic polar valence notation in the formulas and reactions of compounds. Quotations from a recently received letter are quite pertinent to the issue. Professor Stieglitz states:

Like yourself, I would insist on emphasizing polarity in organic (and inorganic) compounds whenever the actual chemical behavior of compounds indicates polarity. I believe, however, that a great deal of confusion would be avoided if we could agree to distinguish the polarity resulting from completely transferred electrons as *ionic polarity* and the polarity resulting from the definite approach of electron doublets to given atoms as *doublet polarity* or simply *polarity*. While in many cases the two may approach each other (as in acetic acid but not in sodium acetate), nevertheless their average behavior makes so profound an experimental difference that it would be a mistake, I believe, not to recognize the difference. Organic chemistry itself would be benefited thereby . . . . for instance in the matter of *tautomeric ions* of certain salts. Besides, failing to recognize and express the difference, we let outsiders condemn the whole question of polarity in organic compounds, because they think we mean ionic polarity in all cases when we certainly have something quite different in mind for alkyl halides, carbonyl derivatives, benzene derivatives, etc. Further, I think it is important to differentiate the two types in our symbols. I have urged . . . . a convention that the charges on ions be put in heavy type . . . . so that we could use ordinary type to indicate polarity in organic compounds, which is so essential for the modern theories of organic chemistry and for teaching much of it from the point of view of scientific theory

rather than of empirical rules. . . . It would do away at once with a great deal of misunderstanding on the part of physical chemists, which is the chief obstacle in the way of progress in this subject in our own country. It was on account of the lack of such a convention that, for instance, Lewis misread my "The Electron Theory of Valence as applied to Organic Chemistry" published in 1922. It stated explicitly at the outset that the Lewis-Bohr doublet theory of union of atoms is accepted as far as the nature of the bond is concerned . . . but insisted on polarity resulting from the definite approach of doublets to certain atoms. Because the ordinary plus and minus signs were used, the article was read by physical chemists, including Lewis, as if ionic polarity were represented.

Stieglitz continues further

As to the validity of our views on definite polarity in organic compounds as well as in many inorganic compounds supposed to be non-polar, I believe there can be no doubt in the minds of men who have actually worked with such substances and are familiar with their behavior. In the inorganic field, the striking difference in behavior of phosphorus trichloride and nitrogen trichloride are consistently and simply explained from the same point of view, Lewis notwithstanding. It is needless to say, in conclusion, that the theories of atomic structure would lead us to expect polarity as the result of the differences in positive kernels of atoms, which will lead to different forces of attraction for doublets. J. J. Thomson (20) develops this relation for methyl chloride in his "The Electron in Chemistry." In benzene derivatives,  $C_6H_5X$ , the influence of X, as  $X^+$  or  $X^-$  is the key to the understanding of their behavior, a fact which, in its naked simplicity, you were the first to recognize and emphasize. I believe they act simply by attracting or repelling the bonds of the ring carbon atoms and have accumulated further evidence to that effect.

Let me conclude by an appeal to your sense of admiration for simplicity by reemphasizing the opinions of the authors I have been privileged to quote, namely that *pragmatic chemists* are more vitally concerned with the adoption of a system of electronic valence notation which is primarily designed to indicate and correlate the actual chemical behavior of the atoms and the radicals of the molecule as displayed under specific experimental conditions

than with the imposition upon structural formulas of an electronic system of notation which is complicated by metaphysical speculations involving the unsolved problems of the constitution of the atom and the disposition of the hypothetical electron shells or the elusive electron orbits of its valence electrons.

Please do not regard these pragmatic points of view relative to questions of atomic structure and to the elimination of octet and electron doublet valence notations from the structural formulas of organic and inorganic compounds as derogatory or prejudicial. Their purpose is to stress a growing opinion among pragmatic chemists that much of the modern speculation is, at the present stage of our knowledge, an uncalled for and undesirable appendage to the systems of chemical formula notations.

Furthermore, it is not paradoxical for pragmatic chemists to advocate and employ metaphysical speculation, which within its proper limits is the soul of science, for, philosophically speaking, many of us believe that all science is metaphysics and necessarily so because, first, there is no such thing as a final explanation in any science; and, second, all science is established on empiricism only by and through sensation experience. Sensation experience is impossible without consciousness, and consciousness has never been defined by any philosopher, psychologist, or behaviorist.

Our present status with respect to our knowledge of the ultimate constitution of matter, that is of the atom, and the related nature of valency, was described in some lines written nearly two hundred and forty years ago, as follows:

Man doth with dangerous curiosity,  
These unfathomed wonders try;  
With fancied rules and arbitrary laws,  
Matter and motion he restrains;  
And studied lines and fictious circles draws;  
Then with imagined sovereignty,  
Lord of his new hypothesis he reigns.  
He reigns; how long? 'till some usurper rise;  
And he, too, mighty thoughtful, mighty wise,  
Studies new lines, and other circles feigns.

Accordingly, while other circles are being feigned, the pragmatic chemist is disposed to advocate some such simple system of polar-

ity valence notation, as indicated in this paper, to correlate structural formulas and chemical behavior; and thus he prefers to avoid the imposition upon his structural formulas of unnecessary and irrelevant complications which, at the present status of his knowledge of the constitution of the atom, are more likely to confuse than to elucidate.

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