

ELEMENTS WITH ANOMALOUS VALENCES¹

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OLDER HISTORY

Kekulé, who derived his ideas of valence largely from the study of carbon compounds, concluded that valence of all elements, as he found it to be in the case of carbon, is a fundamental property of the atom as invariable as the atomic weight itself. Very soon, however, it became apparent that Kekulé's position was not tenable, but that, as Frankland had suggested, valence, with some elements, is not fixed but variable. None the less, the fixed quadrivalence of carbon was accepted and for nearly half a century this idea remained the basis and the principal guide for all work in the vast field of organic chemistry.

With the enunciation of the periodic law, the mooted question of the variable character of valence received, so it seemed at that time, its answer from the periodic table of the elements. It became obvious that, generally speaking, the first three groups show a distinctly fixed valence capacity, from 1 to 3 respectively; in the fourth group the elements are equally divided between those with unvarying quadrivalence and those which can function with a valence lower than four. Beginning, however, with the fifth group, practically all the elements were judged to possess variable valence, ascending in number to 5, 6, 7, and 8 respectively, or descending to 3, 2, 1, according to whether oxygen or hydrogen was the measure of valence.

And yet, a certain regularity was read even into the variation itself. In the carbon group, the elements tin, lead—and later also germanium—were found to function either as quadrivalent

¹ Read in connection with the award of the Willard Gibbs medal at the meeting of the Chicago Section of the American Chemical Society, May 22, 1925.

or bivalent, but not trivalent. In the fifth group the variation was again by two, as As^{III} and As^{V} , and so in the oxygen group, as S^{II} , S^{IV} , and S^{VI} , and finally in the halogen group, where the valence is 1, 3, 5, and 7. Exceptions to this general rule were not unknown, as for instance TiCl_3 and NO , but they were so few in number as to be disregarded. There was known, in addition, a large class of compounds the existence of which could not very well be explained solely on the basis of atomic valences. These complex compounds,—hydrates of salts, double salts, etc.—were looked upon as “molecular compounds,” in which normal molecules were held together not through atomic valences, but through some other force, through “molecular” attraction.

RECENT HISTORY

Such was the state of the valence idea some thirty years ago, when several new, independent, and diverse currents of thought were initiated which finally brought about a profound change in the views concerning the immutability of valence. Only some of these currents can be mentioned here.

COÖRDINATION THEORY

Werner's “Coördination Theory” assumes that in all the complex salts, the hydrated salts, the basic salts, and even in such simple compounds as NH_4Cl , the molecule is made thus: The principal atom is located in the center and around it are symmetrically packed, or “coördinated” a certain number of other atoms or groups, and each of the coördinated units is directly united to the central atom. Usually the coördination number is 6 and these 6 coördinated atoms or groups occupy the six corners of an imaginary octohedron; less frequently the coördination number is 4, and still less, 8; but it may also be 1, 3, 5, or 7, depending upon a variety of factors. In addition to the coördinated atoms or groups which are situated in the immediate vicinity of the central atom, the molecule contains several additional atoms or groups. These however must lie outside of the coördinated complex, since they may become readily dis-

sociated away as ions from the complex. They lie, therefore, in a secondary zone, and the coördinated complex functions in respect to them as a single unit or ion. The following instances will serve as illustrations: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, $[\text{CdI}_4]\text{K}_2$, $[\text{SiF}_7](\text{NH}_4)_3$, $[\text{Mo}(\text{CN})_8]\text{K}_4$ etc.

In the desire to make the new views compatible with the teachings of the older valence hypothesis, Werner attempted to differentiate between the "true" valences of the central atom, as predetermined by its position in the periodic table of the elements, and those new additional valences which the atom presumably acquires in the formation of the coördinated compound. He named them accordingly principal or primary valences and auxiliary or secondary valences. Later, however, this distinction was found to be too indefinite, and with the recognition of the electronic nature of all valence phenomena, the artificial division into auxiliary and principal valences had to be abandoned. The successful application of the coördination theory in the classification and the study of thousands of inorganic and of many organic compounds is evidence that the theory contains a truly important generalization. Moreover, the theory withstood the same severe test to which the stereochemical theories in organic chemistry had been subjected, namely,—the ability to predict the definite number of space isomers possible as well as the particular circumstances essential for the occurrence of optical isomerism in this group of inorganic compounds. The fact that the theory lends itself with only slight modifications, to a restatement² in terms of the modern electron valence theory, is further evidence in favor of the essentially sound basis upon which the coördination theory rests.

What then is the operating valence of the central atom in these coördinated compounds? If we assume, as we must, that there is no intrinsic difference between the principal and the auxiliary valences within the coördination complex, then obviously the active valence of the coördinating atom is the same as its coördination number, and is, consequently, nearly always greater

² (a) J. J. Thompson, *The Electron in Chemistry*, Franklin Institute, 1923; (b) G. N. Lewis, *Valence*, The Chemical Catalog Company, 1923.

than the regular orthodox valence.³ Thus, among the many important consequences of this theory, the following one is particularly apposite in the discussion of the mutability of valence: We have become accustomed to the idea that the valence capacity of an element is not delimited by the position of the element in the periodic table, but that it is a distinctly variable function and can rise to a much higher number than we have ever supposed in the past that it could do.

VALENCE ELECTRONS

Of course, the greatest influence upon the chemist's views of valence came from the revolutionary transformation of the physicist's ideas concerning atomic structure, which transformation was initiated, among other causes, when J. J. Thompson in 1897 determined the mass of the electron, and showed that the nature of the electron is always the same from whatever element it may come. There is general agreement on the main point. In the center of the atom is a nucleus of positive electricity, and surrounding this an equal amount of negative electricity which is carried by electrons as many in number as is represented by the atomic number of the element. Only those electrons, however, which lie in the peripheral zone are directly engaged in the establishment of chemical bonds between two atoms—these alone are the "valence electrons." The number of valence electrons in the elements is a periodic function of the atomic numbers and varies from 0 up to 8, and the elements which occupy corresponding positions in the periods contain an equal number of valence electrons. Eight therefore is the maximum number of valence electrons, and this represents the most stable configuration. So chemical reaction, union among atoms, must tend

³ Werner originally postulated that those groups which are located within the complex are linked each directly to the central atom by principal or auxiliary valences, while those in the secondary zone, always by principal valences either directly or indirectly to the central atom. This postulate, coupled with the statement that auxiliary valence is unable to effect the union of univalent radicals, may lead one to the somewhat ambiguous interpretation that the central atom in some instances assumes a valence even greater than that represented by the coördination number of the atom. See for instance the formulas in Thomas' "Complex Salts," Van Nostrand, p. 22, 1924.

towards the establishment of a sphere of eight valence electrons around the atoms which participate in the reaction. But even with the allowance that the valence electrons alone and no other electrons are concerned in the creation of chemical bonds between atoms, there still arises a multitude of perplexing questions when one tries to picture to himself the *modus operandi* of this process. If an active bond is created through the complete transference of one valence electron from atom A to atom B, then evidently the maximum bonding capacity of atom A is determined by the number of its valence electrons, and there is no inherent reason why atom A should not exhibit, under specific experimental conditions, every possible variation in valence between its maximum and zero. The same applies to the second atom in this transaction, the operative valence of atom B being measured by the number of electrons it has acquired from atom A. On the other hand, if it be assumed that a chemical bond can also be established when atoms share electrons, be it either in the statical or the dynamical sense, then the question arises how many electrons must be thus shared for each bond, how many atoms may partake simultaneously in the sharing of the same electrons. It becomes impossible to predict the maximum bonding capacity of an atom unless some arbitrary postulates be introduced which would limit the variable factors mentioned. G. N. Lewis and Kossel, have advanced the happy postulate that a bond consists of a *pair* of shared electrons, shared only by *two* atoms. With this postulate the hypothesis of shared electrons has proven exceedingly useful. And yet one wonders why one electron cannot be shared by two or more atoms; one wonders whether the active triatomic hydrogen

may not have the structure $\begin{array}{c} \text{HH} \\ \vdots \\ \text{H} \end{array}$. May not the molecule of phosphorus, P_4 , be $\begin{array}{c} \text{P} \cdot \cdot \text{P} \\ \text{P} \cdot \cdot \text{P} \end{array}$? If the author reads him correctly,

J. J. Thompson assumes the existence of bonds of some such nature in the hydrated salts, polymers of formaldehyde, the possible existence of unstable $(\text{CaCl}_2\text{Cl})^-$.⁴

⁴ See the very suggestive critical review in Main Smith's "Chemistry and Atomic Structure," Ernest Benn, Chapter XIII (1924).

Accept whichever view of valence mechanism we wish, it is now obvious that the idea of fixed valence for some elements and variable for others is untenable. Every element must be capable of forming compounds through the operation of all its valence electrons, or through the operation of only some of these. Experimental conditions alone must be the determining factor whether a given element will act in its maximum capacity, in some particularly stable valence, or in any other supposedly anomalous valence.

TRIVALENCY OF CARBON, FREE RADICALS

It would be desirable to point out in this connection still other important recent factors that have contributed materially towards the development of our views concerning the mutability of valence capacity. The exigencies of the present occasion, however, make this impossible within the time limitation, since, by all precedent, it is incumbent upon the speaker to say something of his personal contribution in the field under discussion, be that contribution, as it is in this case, ever so slight.

With the discovery, in 1900, of the curious substance which has become known as triphenylmethyl, the idea of fixed valences received a very serious set-back. Here was a substance which, according to all standards of experimental evidence, behaved as if it contained one of its 19 carbon atoms in the molecule in the trivalent and not quadrivalent state. It constituted the first definite example of anomalous valence in the behavior of the very element that had, up till then, shown an unvarying constancy in the tens of thousands of its compounds. Many other similar compounds have been prepared since,—not far from a hundred triarylmethyls—and the “trivalence” of carbon is now looked upon as a normal manifestation, for we know fairly well when to expect it and how to recognize it when it does occur. In the early discussions, the historical interest of these substances was emphasized rather than their theoretical bearing. The implied existence of a substance with a carbon atom in trivalent state, was equivalent to stating that an uncompleted molecule can exist, or, in the older language, that a “radical” is a reality and not

merely a symbol and a figment of the imagination. It brought back to memory the bitter controversies of the long forgotten past. It recalled the stirring events in the history of chemistry when Gay-Lussac, in 1815, announced the preparation by him of free cyanogen, in which, so he thought, he obtained the first true "compound element" or radical, and that he thus vindicated Lavoisier's prediction of some 30 years prior. It recalled the days of Liebig and Wöhler's investigation in 1832, of the "benzoyl" radical; the vigorous and at times somewhat one-sided participation of Berzelius in these controversies, of Berzelius the law-giver in the chemistry of his times. It recalled the joint proclamation of Liebig and Dumas, in 1837, who professed to see locked up in these radicals the very mysteries of organic nature. It brought back to memory the discovery by Bunsen in 1842 of the presumed radical "kakodyl;" by Kolbe, in 1849, of "methyl," and by Frankland, in 1850, of "ethyl" and "amyl." It recalled the passionate and caustic expressions of Gerhardt and of Laurent in their bitter opposition to the theory that radicals can exist; it recalled, finally, the fading away of that theory with the advent of the valence hypothesis and the general acknowledgment at that period of the invariable quadrivalence of carbon, so strenuously advocated by Kekulé.

ANOMALOUS VALENCE IN SOME OTHER ELEMENTS

This represents the historical aspect of the triphenylmethyl episode. A more permanent significance of the triarylmethyls as a class lies in the fact that the study of these compounds has opened the way for analogous studies also with elements other than carbon. By means of methods that are similar to, or not much different from, those which have been employed in the preparation of the free triarylmethyl radicals, it has been fairly well established, through the labors of many investigators,⁵ that compounds can exist which contain an atom of the following elements in an anomalous state of valence: N^{II} , N^{IV} , S^I , O^I , Si^{III} , Sn^{III} , Pb^{III} . We know now all kinds of free radicals.

⁵ See full reviews: (a) Schmidlin, "Triphenylmethyl," Ferdinand Enke, 1914; (b) Walden, "Chemie der freien Radikale, S. Hirzel, 1924; (c) Gomberg, *Chemical Reviews*, I, 91-141 (1924).

INSTABILITY OF FREE RADICALS

It is not surprising that the existence of such free radicals has been overlooked for so long. They are among the least stable substances and would be destroyed under conditions which ordinarily prevail in synthetic work. Thus, for instance, the triarylmethyls unite with oxygen as greedily as does yellow phosphorus; they are very susceptible to reducing agents and to oxidizing agents; they unite instantly with iodine and bromine; they are sensitive even to traces of mineral acids; light affects them; even very gentle heat destroys many of them; they undergo spontaneously intermolecular oxidation and reduction; some show the tendency to unite with every possible solvent in which they are dissolved, and the different types of radicals unite with each other, as for instance $(C_6H_5)_2N \cdot CR_3$. But now, with the recognition of their extremely unstable and unsaturated character, the free radicals are readily prepared and their individual characteristics can be determined.

Obviously, the unsaturated character of the C, or N, or O, as the case may be, must impart to these odd molecules a great tendency to pair up among themselves and thus bring into play their unused, or unshared, valence electrons. And such indeed is the case. Seldom if ever is this tendency towards association entirely wanting. In by far the largest number of cases we have to remain satisfied with an equilibrium of this nature:

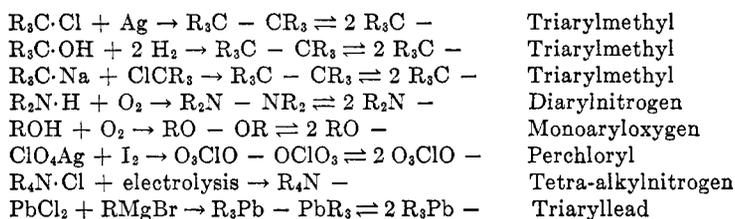


This equilibrium has been found to shift in favor of the dissociation phenomenon with slight changes in the conditions of the experiment. Rise of temperature or increase of dilution augments the amount of dissociation of the dimolecular compound into the monomolecular free radicals. But, above all, the nature of the groups around the central atom exerts the greatest influence upon the degree of dissociation. So slight a change as the substitution of $(CH_3O \cdot C_6H_4)$ for (C_6H_5) increases enormously the extent of the dissociation of all radicals in the C and N series. In fact, three such groups on one carbon atom induce practically

100 per cent dissociation. There are other groups of similar influence, such as biphenyl, naphthyl, etc. It is still too early to make wide generalizations in this respect, we have to remain satisfied with a few meager empirical deductions. Hence, when we speak of free radicals, we always mean radical, in equilibrium with a certain amount of the undissociated completed molecules wherein the two radicals bring into exercise their full quota of valencies.

METHOD OF PREPARATION

The following equations will illustrate some of the typical methods which have been employed by various investigators for the preparation of these compounds. The reaction, in nearly all cases, must be carried out in strictly anhydrous solvents, and in absence of oxygen.



VALENCE OF ELEMENTS IN GROUPS I-III

A glance at the periodic table shows in what direction the experimental evidence has progressed. Starting with carbon in Group IV, practically all the elements in that group have been shown to act not only as quadrivalent or bivalent but also as trivalent. Then, one after another, representative elements from the groups to the right of carbon were also found to function with anomalous valence capacity. Nothing, however, of similar nature has yet been done with the elements to the left of the carbon group—almost one-half of the periodic table still remains, in this sense, uncharted sea. To quote from G. N. Lewis:⁸ "It is a remarkable fact concerning the metals that we have so far discussed that when they form ions they give off simulta-

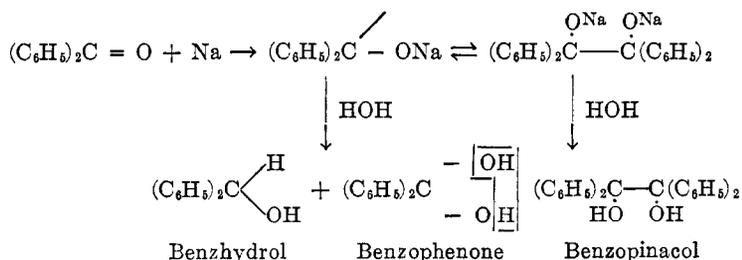
⁸ Reference 2, (b), p. 61.

neously all of the electrons of the outer shell. When Ca acts as an electrode in electrolysis, its atom never loses a single electron to form the ion Ca^+ . If it does, this ion must be unstable and react immediately according to the equation, $2 \text{Ca}^+ = \text{Ca}^{++} + \text{Ca}$. . . Compounds of the type CaCl are unknown. Aluminium does not form the ions Al^+ and Al^{++} , nor are compounds known of the type AlCl and AlCl_2 . In other words, when such a metal reacts it uses all of its valence electrons or none."

It is therefore with no little trepidation that I undertake to report at this time some experimental evidence, meager as it still is, which seems to indicate that valence may become a variable function in some of these metals.

PROBABLE EXISTENCE OF MAGNESIUM-MONOHALIDE

It has been a well-known fact that when benzophenone, dissolved in perfectly dry ether, is treated with metallic sodium, reaction occurs without displacement of any hydrogen, and an intensely colored addition product is formed. When now this addition product is decomposed with water, there is formed, among other products, benzopinacol. Schlenk, in 1911, re-investigated this reaction thoroughly and showed that practically all aromatic ketones make similar addition products with metallic sodium, potassium, and lithium. More recently, F. F. Blicke has made some additional observations in connection with this reaction. The reaction which occurs has been formulated as follows:



The strongly electro-positive character of metallic sodium, the tendency of the sodium atom to part with or share its single

valence electron, causes the establishment of the bond between the oxygen atom of the C = O group and the sodium atom. As a consequence of this, the carbon atom becomes now trivalent, as it is in the triarylmethyls, and this free radical is undoubtedly in equilibrium with its more stable dimolecular form. If such a mixture is now hydrolyzed it must yield, among other products, some pinacol.

Recently, in connection with carrying out a Grignard reaction, an observation was made in our laboratory that metallic magnesium, which has been activated by means of iodine, reacts to some extent with benzophenone and small amounts of benzopinacol result, a phenomenon which has been noticed previously by others,⁷ but for which no adequate explanation has been given. Jointly with Mr. W. E. Bachmann we have followed up this reaction and have obtained these results:

1. Magnesium powder as such, or even if amalgamated, does not react with benzophenone in ether or benzene, contrary to the statement in the literature.

2. Magnesium which had been activated by the addition of iodine or bromine does react with benzophenone. A gram atom of halogen for one mole of ketone gives in a short time practically 100 per cent yield of pinacol, even when the reaction is carried out at room temperature.

3. Magnesium iodide, in ether or benzene, combines with benzophenone in the proportion $\text{MgI}_2 \cdot 3(\text{C}_6\text{H}_5)_2\text{CO}$, but even on prolonged boiling of the mixture, no benzopinacol is formed.

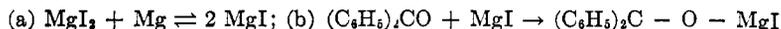
4. When to a suspension of the above double compound in ether or benzene, powdered magnesium is added and the mixture is heated for a short time, reaction occurs and the pinacol salt is produced.

It is evident therefore that neither metallic magnesium alone, nor magnesium iodide alone, can accomplish the reduction of the ketone to the pinacol. It requires the simultaneous action of the two. What other unsaturated substance can there be formed in the reactions $\text{Mg} + \text{I}_2$, or $\text{Mg} + \text{MgI}_2$, that will function exactly as does metallic sodium, if it be not MgI ? The one still

⁷ (a) Schmidlin, *Ber.* **39**, 4202 (1906); (b) Schlenk and Thal, *Ber.* **46**, 2847 (1913).

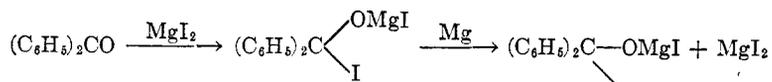
unpaired valence electron in the magnesium atom of such a compound would correspond to the one valence electron in metallic monatomic sodium. Moreover, the MgI should have the added advantage over the sodium in that it is likely to be soluble, as MgI_2 is, in ether or benzene, and consequently the speed of our reaction with benzophenone should be faster than in the case of metallic sodium. Experiment verifies this—the reduction is quicker and the yield is ever so much better. We have tested out this reaction on some 10 aromatic ketones with surprisingly good yields of the corresponding pinacols.

It could hardly be expected that more than a minute amount of the MgI could be present at one time. The equilibrium in equation (a)



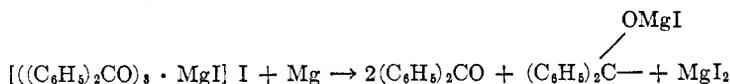
is no doubt preponderantly in favor of the left hand side of the equation. If, however, a ketone be present it will use up what little there may be present of this unsaturated active compound, (Equation (b)), and consequently more and more of magnesium monohalide will be produced. The restoration of the equilibrium proceeds quite rapidly. An appreciable amount of the ketone is reduced within the first few minutes.

Other interpretations of this unique reaction have suggested themselves, which are not so radical as the one given above, as for instance:



The compound with the trivalent carbon atom will then double up and upon hydrolysis pinacol will result. Or, with the coordination number for magnesium as 4, one may assume the possible formation of the coordinated compound as indicated in the equation below. The metallic magnesium would now remove the one atom of iodine in the secondary zone, and then, because of the increased affinity content of the magnesium atom

within the coordination complex, the compound $(C_6H_5)_2\overset{\diagup}{C}OMgI$, the precursor of pinacol, would be formed:



If either of the two suggested mechanisms be correct, then substitution of molecular silver for the metallic magnesium in the second step of the reaction should give better if not equally good results. There is no reaction at all when metallic magnesium is replaced by metallic silver.

Our tentative hypothesis is, therefore, that MgI is the reducing substance in this reaction. This new reducing agent has been tested out on aromatic aldehydes and esters, and the results indicate that its action, although more complicated than with ketones, is strictly parallel to that of metallic sodium.

It may be mentioned in this connection that a number of inter-metallic compounds have been described by Desch wherein Mg seems to function as univalent, such as $AlMg_3$, $SnMg_2$, and $AuMg_3$.⁸ May not the enhanced activity of amalgamated magnesium be due to the formation of some $HgMg_2$ and not merely to the fact that the magnesium in solution becomes more certainly monoatomic?

It might be added, that cadmium and zinc have given no indication of forming monohalides under conditions similar to those used with magnesium. Beryllium has not as yet been tested.

To sum up then, indications have been obtained that magnesium may be forced to function as univalent, in distinction from its normal bivalent state. One may hope that similar methods of attack with other metals may yield more decisive results.

CONCLUSION

And so, on the one hand, the study of complex inorganic compounds has led to the conclusion that the valence of many

⁸ Dean, "Theoretical Metallurgy," J. Wiley and Sons, p. 81 (1924). For the very active alloy $PbMg_2$, see Ashcroft, *Trans. Faraday Soc.*, **14**, 276 (1919).

elements may become higher in number than their normal. On the other hand, the study of some complex organic compounds, of the so-called free radicals, proved that some elements may function with anomalous valences, lower than their normal. Concurrently, the physicist, through the momentous advances in the knowledge of atomic structure, has supplied the chemist with a logical concrete picture of the cause and the mechanism of valence manifestation. That picture predicates that, as a matter of course, valence for all but the inert elements must be variable and not fixed.

One may be pardoned, I hope, for attempting to view from this special angle some of the classic experiments of recent times. The determination, by the x-ray method of analysis, of the crystal structure of diamond by Bragg and of graphite by Hull, and by Debye, suggests that in diamond the carbon atom is quadrivalent, but that in graphite the fourth valence is weakened very much, even if not quite to extinction. Again, the positive-ray method of analysis indicates the production from CH_4 of univalent ions: C^+ , $(\text{CH})^+$, $(\text{CH}_2)^+$, which proves that the carbon atom in these is univalent, bivalent, and trivalent, respectively, assuming that the positive charge is acquired through loss of a valence electron. By the same method of analysis, according to J. J. Thompson, Hg functions, from Hg^I to Hg^{VIII} .⁹ And when Millikan has stripped by explosive sparking some elements of all their valence electrons, the atoms pick these up again, not all at once, but one by one,—do not these results also indicate variability of valence capacity?

⁹ F. W. Aston, "Isotopes," Edward Arnold & Co., p. 64, 72 (1922).