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SOME REFLECTIONS CONCERNING VALENCE VARIATION AND ATOMIC STRUCTURE[1]

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Permit me, please, to offer a word of explanation concerning the choice of the subject for this evening's talk. Many years ago it fell to my lot to become interested in a striking instance of valence variation, and the solution of that problem rested wholly on experimental laboratory evidence. A number of other similar cases of valence variation have been subsequently encountered by various workers, and their conclusions, also, rested on experimental evidence. Meanwhile, during the last ten years, and especially during these last five years, the theoretical aspect of the entire valence question has received much clarification as a result of certain theories based on the spectroscopic study of the elements. The question is alluring—do the empirical findings, in this branch, of the near past harmonize with the recent theoretical deductions? Obviously, the nature of the reply to this question will be colored to some extent by the psychology of the questioner, but the correctness of the answer can only be in proportion to the requisite technical training possessed by the inquirer. On that last score, I bespeak your generous indulgence.

The Karlsruhe Congress

To-morrow, September 3, will mark the seventy-first anniversary since the occurrence of the interesting gathering of chemists, in 1860, in the peaceful little city of Karlsruhe, Baden. The delegates came from all countries in Europe, in response to an invitation sent out by a self-appointed committee. Among the 45 signatures attached to the invitation were those of Liebig, Wöhler, Bunsen, Frankland, Williamson, Pasteur, Dumas, but the moving spirit of the organization was young Kekulé. The object of the meeting was to see if by exchange of opinions some reasonable agreement could be reached in regard to the precise

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[1] Address of the president, the American Chemical Society, Buffalo, N. Y., September, 1931.

definitions of the concepts atom, molecule, equivalent, atomicity, etc. Not all the original signatories to the invitation came to the meeting. Among the some 130 in attendance, Bunsen was present, with the spectroscopic discovery of caesium only a few months old. Dumas, Stas, Marignac, Friedel, Wurtz were there. Of the much younger men, one may mention Roscoe, Wislecenus, Beilstein, Erlenmeyer, and also young Adolph Baeyer, 25, a privat-docent fledgling and eager for some kind of position.

It was at the last session of the meeting that Cannizzaro urged upon his hearers the adoption of the long neglected, fifty-year old hypothesis of Avogadro as the only safe guide for differentiating between atom and molecule, as the only safe basis for establishing atomic and molecular weights. Within the next few years Cannizzaro's tables of atomic weights were much in use. This proved to be an important factor in the successful development of the valence hypothesis, since the hypothesis depended for its conclusions upon the relation between equivalent and atomic weight.

VALENCE VARIATION

The question, whether a given element possesses a fixed or variable valence, came at once to the front and continued to serve for many years as a perennial topic of bitter disputes. Kekulé, having been so very successful in his development of structural organic chemistry by attributing to carbon an unvariable valence of 4, made up his mind that all other elements must have each some definitely fixed and unalterable valence. Henceforth he remained committed to this point of view, insisting that valence, like the atomic weight, is an unchangeable attribute of an atom. In order to explain away the existence of such compounds as NH_4Cl or PCl_5, he brought forward his well-known view of molecular compounds. Ammonium chloride, in Kekulé's language, was a combination of the molecule NH_3 and the molecule HCl, held together not in virtue of an increase in the valence capacity on the nitrogen atom from 3 to 5, but in virtue of some kind of attraction betwen the two molecules. This notion of molecular, in distinction from true atomic, combination has been handed down from generation to generation with such slight modifications of meaning as are implied in the terms molecular complex, residual affinity, auxiliary valence, coordination number, etc.

After all, the question of valence variation for one and the same element was but a part of a much deeper mystery. Why do the *various* elements differ among themselves in combining capacity? How far can this difference extend? A partial answer to this query was supplied by the revelation that all properties of the elements, including that of valence, appear to be periodic functions of the atomic weights, repeating themselves after each little group of seven or eight elements, if the elements be arranged in the order of their atomic weights. Biographers like to trace the inception of the Periodic Table, directly or indirectly, to the Karlsruhe meeting in 1860. Be that as it may, both L. Meyer and young Mendeleeff were present at that gathering and both became ardent disciples of Cannizzaro's reforms. It may not be without interest to mention that in his first paper (1869) Mendeleeff did not include valence as a periodically recurring property of the elements, but a year later, in his second and more complete paper, valence appears as the most important periodic function, being successively 1 to 7 for the seven groups, or 1 to 8 if we include also the iron-cobalt group. And ever since, valence has retailed its importance in the periodic classification of elements.

Mendeleeff was aware that he could make valence a strictly periodic property, provided the oxygen derivatives of the elements are considered and not their hydrogen derivatives. In the third period, for instance, we have a clear-cut procession of valence from one to that of seven: Na_2O, MgO, Al_2O_3, SiO_2 P_2O_5 SO_3 and Cl_2O_7. If the valence of these same elements be measured by their hydrogen derivatives—the picture changes. The first three vertical groups in the periodic table give no stable hydrides, the fourth group indicates, again, quadrivalence, but groups V, VI and VII indicate a successively decreasing instead of increasing valence, namely, 3, 2 and 1, as for instance in PH_3, SH_2, ClH. Thus the periodic table in a way confirmed the contention of the earlier chemists that valence of elements can not be considered as fixed, for it seems to vary with the nature of the measuring element, whether the latter be oxygen or hydrogen. Moreover, some of the elements, even in group IV, were known not to be exempt from valence variation towards one and the same element—*i.e.*, titanium forming compounds $TiCl_2$, $TiCl_3$ and $TiCl_4$: tin and lead being di- as well as tetra-valent.

DEFICIENCY VALENCE

Gradually it became tacitly recognized that as a rule the elements do conform to their group position in the periodic table as regards their maximum valence; and then it was further assumed that some elements do not always exercise the full limit of their valence capacity, this being especially the case with the nonmetals. The hunt for the possible occurrence of deficiency-valence became a frequent subject for experimentation, and this search extended well into the present century. Thus, the claim has been made repeatedly that sub-oxides with anomalously low valence result when the oxalates of certain metals are heated at 200–300° C. Moissan, in 1899, mentions that metallic calcium reduces calcium di-iodide to calcium monoiodide on fusing together the mixture of the di-iodide and the metal. Haber found that barium monochloride resulted from the electrolysis of barium dichloride at 500–600° C. Calcium monochloride has been prepared crystalline, and in remarkably pure state, by heating in small bombs the dichloride with metallic calcium to 1,000° and then plunging the bomb into solid CO_2.

Carbon, more so than any other element, seemed to possess a fixed valence, tens of thousands of carbon compounds, with carbon functioning always as quadrivalent, offering testimony to that effect. When, therefore, it was demonstrated that carbon, also, may on occasions exhibit a deficiency of one valence and function as trivalent, it opened a wide field for search of anomalous valence behavior on the part of other elements. As a result, we now know of the existence of compounds which may contain in their molecules either monovalent oxygen, or divalent nitrogen, trivalent lead or tin, monovalent iron, cobalt, nickel or manganese.

EXCESS VALENCE

To say that deficiency valence results from non-operativeness of the maximum possible potential valence does not of course explain the phenomenon, but at least it makes it not irreconcilable with the postulates of the periodic system. The case, however, is different when we come to consider that large class of complex compounds which result from combination of several whole and completely saturated molecules. Take the very simple example, $K[Ag(CN)_2]$. When dissolved in water, dissociation occurs and there are formed the ions K^+ and $[Ag(CN)_2]$.—Evidently, the atom of silver in the anion is functioning as if it were divalent. Similarly, in $K_2(HgI_4)$, Hg is apparently quadrivalent; in $K_4Fe(CN)_6$ the atom iron is hexavalent. In order to obviate, or at least to soften, this discrepancy between valence as ordinarily understood and the peculiarly high valence of the elements in these complex substances, Werner called the latter kind of valence "coordination number."

Obviously, for an adequate explanation of both aspects of valence variation, deficiency and excess, there is required something more than merely the knowledge of the quantitative manifestation of the valence action. A knowledge of the nature of the causative agent of valence, and of the mechanism involved in the action of that agent, are essential. The disclosures of atomic structure are gradually supplying the knowledge of these two factors.

ATOMIC STRUCTURE

Mendeleeff survived by almost ten years the establishment of the doctrine that the electron is a constituent common to all elements. It would be interesting to learn what was Mendeleeff's reaction to this epochal discovery of Thomson's, since Mendeleeff himself had repeatedly insisted that "the periodic law affords no indication of the unity of matter or of the compound character of the elements." What a striking change in our cosmic views in so short a period! That all matter is electric in its nature is now a fundamental tenet in modern science.

The Rutherford-Bohr planetary atom, with its positively charged nucleus surrounded by the negatively charged electrons, has reached, as you know, that astounding stage of development when one may speak of the structure of the atom with a reasonable degree of confidence. Still, for one whose detailed knowledge of the subject is not of that extent when familiarity with the subject shields one against surprises, for such a person there is something terrifying in the boldness of the statement, however well founded it may be, that a single atom of mercury consists of 400 individual units, and that its 200 electrons can be arranged into at least 15 groups in accordance with their respective specific functions in the atom in its normal state. Still more astounding is the statement that in a single atom two electrons can never coincide in all their energy relations to the atom.

This is not the occasion to undertake a detailed account of the theories of atomic structure, and I am certainly not the person qualified to undertake the task. In presenting the following few remarks I shall endeavor to observe Mr. Sidgwick's sound advice to the chemist—"not to use the terminology of physics unless he is prepared to recognize its laws."

Basing their deductions upon the study of the manifold series of lines in the optical and the x-ray emission spectra of the elements, and in order to account for these series, the spectroscopists have concluded that the electrons which surround the nucleus can be classed into several principal groups in accordance with their respective energy content. We can imagine, with Bohr, that as the number of the planatory electrons, in the heavier atoms, becomes larger, they arrange themselves in concentric shells around the nucleus, each shell being characterized by its own energy level. The first horizontal series, hydrogen to helium, has one shell, and each succeeding series—whether the series be long or short—acquires an additional shell.

VALENCE ELECTRONS AND VALENCE ACTION

Much detailed knowledge is at hand concerning the exact number and disposition of the electrons in the individual inner shells. The chemist, however, is interested mainly in the outermost electrons, for these alone are affected in chemical reactions between atoms. The elements in the first vertical group of the Mendeleeff-Moseley periodic table are monovalent and contain each one valence electron; the divalent elements in the second group contain 2 such electrons, etc. The inert gases in the eighth group are zero-valent, and are supposed to owe their stability and inertness to the presence of 8 electrons in exterior shell. It is one of the unsolved mysteries—or one of the arbitrary postulates, as you wish—that an exterior shell, no matter how many other shells happen to interpose between it and the nucleus, becomes stabilized by the presence of 8 electrons, while shells three and four, counting from the nucleus, may contain, and for full stabilization actually require, 18 and 32 electrons, respectively. The great acumen with which G. N. Lewis and also I. Langmuir, two pioneers in this field, have expounded this theory of a stable 8-electron shell, and also the application of this theory to molecular structure, is recent history to all of us.

It is customary to distinguish three kinds of valence action: (1) When each of the two combining atoms contributes a valence electron and the bond consists in the two atoms sharing the pair of electrons. This conception is almost identical with the original notion of the bond as has been used in organic chemistry since the days of Kekulé, except that the idea is now put in modern nomenclature. Such a bond is said to be non-polar or co-valent. (2) An atom may be completely robbed of one of its valence electrons, and so becomes a positively charged ion; (we may call this a positive valence). (3) The atom may gain an electron from some other atom, and become a negatively charged ion; (this we may designate as a negative valence). The last two modes of valence action are generally grouped together as electro-valence, since they both result in the establishment of a polar bond, *i.e.*, the two oppositely charged ions being held in loose combination through electrostatic attraction. However, for the purposes of the present discussion it seems preferable to class all three modes of valence operation into one group, *i.e.*, the so-called electro-valence bond involves also the participation of a valence electron from each of the atoms that are held by the electro-static attraction. A word of explanation seems necessary. For some time I have been a slave to the idea that an electro-valence bond is a secondary, and never a primary result of valence action. The primary phase consists always in the establishment of a pair of shared electrons between two atoms, one electron from each participating atom. Whether the bond remains as so formed, or whether the pair of electrons will shift wholly to one of these two atoms—impoverishing the one and enriching the second atom by one electron—is a matter which depends upon the relative sizes of the nuclei of the two atoms, and upon many other circumstances. For instance, hydrogen chloride, liquefied, is not an electrolyte, and hence the bond is non-polar; but when dissolved in water, the bond becomes polar and dissociation is almost complete. Many analogous instances may be cited—and one is not wholly unjustified in making the generalization that all bonds are, in their primary phase, non-polar, requiring from each of the two atoms one electron, the two electrons being "corresponding electrons (London, Heitler). The remarks which follow refer therefore to the non-polar, as well as to the primary phase of the electro-valent bond.

DISTRIBUTION OF VALENCE ELECTRONS

Now, there is abundant spectroscopic evidence that the valence electrons are not limited exclusively to the very outermost shell alone. This is particularly true of the elements with atomic weight of 45 and above, and the atoms of which have more than 3 shells. There are almost 20 elements, the valence electrons of which must be considered as distributed, part being in the outer shell and some in the next underlying shell. Moreover, in some rare earths, the distribution of the valence electrons occurs into 3 shells. It stands to reason that elements of this kind must exhibit variable valence. In some chemical reactions the electrons in the outer shell alone may be induced into action, while under other different circumstances valence electrons in the underlying shell as well may become detachable, and thus may also become operative as valence electrons. Such elements are Sc, Ti, Cr, Mn, etc. These elements are well known for their multiple valence.

However, even in those elements where the valence electrons are all contained in the outermost shell only, occurrence of variable valence is still consistent with atomic structure theories. Spectroscopic evidence indicates that the electrons in the outer shell, on the basis of their energy content, fall into two subgroups, 2 electrons in the first subgroup, and the remaining, from 1 to 6, as the case may be, fall into the second subgroup. It is conceivable that, beginning with the third vertical group, where the elements have each three valence electrons, either all three valence electrons in the atom may become operative, or only those that belong to one of the two subgroups, according to particular conditions of chemical reaction. The finding of the still unknown AlCl or $AlCl_2$, in addition to the well-known compound $AlCl_3$, should occasion no great surprise, since the three valence electrons in aluminium are not all in the same subgroup. Indeed, beginning with the fourth vertical group in the periodic table, such variation is known to be rather the rule than the exception, and this behavior is quite in agreement with the postulate of the theory, since the valence electrons, although all in the exterior shell, are distributed among two sub-classes as 2.2, 2.3, 2.4, 2.5, in IV, V, VI, VII periodic groups respectively. Thus, we have $PbCl_2$ as well as $PbCl_4$; PCl_3, PCl_5; SCl_2, SCl_4, SF_6, etc. Of course, not all permissible variations in molecular composition have as yet been realized. For some of these compounds, at the present time still hypothetical, theoretical considerations predict an endothermal and unstable state; other compounds, even if predicted to be thermodynamically stable, are likely to prove less stable than analogous products into which they can readily transform. Thus, AlCl is probably an exothermic compound and should exist, were it not for the fact that $AlCl_3$ is decidedly more stable; consequently, there is a tendency for the following reaction to occur spontaneously: $3\ AlCl = 2\ Al + AlCl_3$.

Thus, the manifestation of valence variation appears explainable in the case of such atoms which have their valence electrons distributed among 2 or 3 shells; explainable also in the case of atoms the valence electrons of which are all located in one shell, but the number of these electrons is more than 2. But how do the following instances of valence variation find their explanation: (1) In the second group metals—Mg, Ca, Sr, etc.—the two valence electrons are both in the same shell and both belong to the same subgroup; therefore, both electrons may be expected to enter into the formation of a bond with equal ease and therefore simultaneously. And yet we know, as cited in the early part of the paper, under certain conditions this is not the case. (2) Carbon, with its 4 electrons as 2.2, may be expected to function as bivalent and quadrivalent—but why trivalent? Similarly, why oxygen-univalent? (3) Why in chlorine, is valence variation by two—1, 3, 5, 7? How to explain the fact that fluorine, a member of the same group with chlorine, is always univalent, and no more?

You would not wish me to enter here upon the discussion of these and other similar questions. May I merely say that, in my judgment, no one can fail to be impressed by the cogency of the arguments which London, Heitler and others have built up during the last three or four years, on the basis of what is known as Pauli's Exclusion Principle. All the above-mentioned valence variations seem to be explainable in a satisfactory manner.

The above few illustrations may suffice to show that modern atomic structure theories are of great assistance to the chemist in explaining valence variation. What used to be a purely empirical fact becomes in the light of these theories an understandable concrete process. The occurrence of compounds with monovalent calcium or magnesium, divalent aluminum, trivalent carbon, and other cases of deficiency valence are not only compatible with these modern theories, but are predictable on the basis of the theories. The situation is not quite so satisfactory when we come to consider the coordination compounds, wherein elements exhibit what looks like excess valence. Nearly all attempts at explanation of these cases of valence variation make wide use of hypotheses, which in themselves may be legitimate and are plausible, but they do not rest on sufficiently clear-cut experimental evidence. It is not surprising, therefore, that two such eminent authorities as Sidgwick and Sugden do not agree whether a non-polar bond always requires for sharing a pair of electrons or whether a single electron will suffice; whether an octet of electrons around an atom is the limit, or whether ten, twelve and more electrons are also possible. The fundamental theory, however, of atomic structure is sound, and we may rest assured that these problems will in time also be solved.

CONCLUSION

In bringing to a conclusion these few scattered reflections concerning valence variation and atomic structure, may I be permitted to say this: He who is experimentally inclined may henceforth take heart and he need not be quite so timid in interpreting strange chemical reactions on the assumption of possible anomaly in the valence of the reactants. The physicist has no hesitation in speaking of the temporary existence, at the higher temperature employed in spectroscopic work, of such molecules as BaCl, AlO, (HO), CH^+, CH_2, MgF, etc. Is it not possible that under the influence of surface forces somewhat similar valence variation may not be excluded even at lower temperatures? That these strange compounds are thermodynamically unstable may be true. Nevertheless, they may function as the mysterious catalysts, or as initiators of chain reactions.

NEW CONCEPT OF EVOLUTION BASED UPON RESEARCHES ON THE TITANOTHERES AND THE PROBOSCIDEANS[1]

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THE new concept of evolution is not to be confused for a moment with the pre-observational "entelechy" of Aristotle, the "vitalism" of Driesch, the "évolution créatrice" of Bergson, the "emergence" of Lloyd-Morgan, the "holism" of Smuts, or any other of the age-long "internal-perfecting" hypotheses which are

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[1] This is the seventh paper on the Origin of Species, and the newer aspects of the Evolution problem. The National Academy of Sciences, November 16, 1931.