

b. Warming gently with dilute caustic soda gives free ammonia. Carbonyldiurea or biuret is decomposed only with difficulty by caustic alkalis.

c. Dilute acids throw down a precipitate which corresponds in its properties to the carbonyldiurea prepared by Schmidt.¹

That carbonyldiurea acts as a dibasic acid was shown by the preparation of its silver salt. A solution of the ammonia salt of carbonyldiurea was added to two molecules of silver nitrate. This formed immediately a fine, heavy, white precipitate, which was filtered, washed with dilute ammonia and hot water, and analyzed.

I. 0.2686 gram substance gave 0.1620 gram silver.

II. 0.1958 gram substance gave 0.1182 gram silver.

	Calculated for $C_3O_3H_4N_4Ag_2$.	Found.	
		I.	II.
Silver.....	60.00	60.31	60.36

The disilver salt is very stable and is discolored only slowly on exposure to the light.

When equal molecules of silver nitrate and carbonyldiurea were mixed no monosilver salt was obtained, but only the disilver compound.

I wish to take this opportunity to thank Prof. Stieglitz for his valuable direction and kindness in the prosecution of this work.

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THE NATURE OF VALENCE.

BY F. P. VENABLE,²

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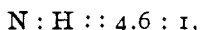
THE term "valence" is variously defined as the "combining capacity", "capacity of saturation", "quantitative combining power", or "chemical value of the atom." It is well known that the introduction of this idea into chemistry was due to the development of the type theory, a system which had at first a purely empirical basis. Sixty years ago there was still some hesitation as to the acceptance of the atomic theory or the need for such a theory. Much use was made of the term equivalent, which had been Wollaston's expedient for avoiding

¹*J. prakt. Chem.* [2], 5, 39.

² Address, as chairman, delivered before the North Carolina Section.

the difficulties arising from the full adoption of the theory of atoms.

Wollaston had been himself very far from consistent in the use of the term. The numbers called by him 'equivalent weights' were not infrequently atomic and molecular weights and fully as hypothetical as the so-called atomic weights of Dalton. In the later use of the term it signified solely the numbers obtained by analysis without the introduction of any theoretical considerations. Thus, on analyzing ammonia, the ratio



is gotten, and therefore the equivalent of nitrogen is 4.6. Strange to say the equivalent given by Wollaston corresponds with the present atomic weight, whereas the atomic weight given by Dalton corresponds with what would be the equivalent.

It is manifest that the idea of equivalents needed something more than the simple theory of atoms to make it clear and tenable. It embodied two distinct conceptions and if we hold to an atomic theory we must introduce a further explanatory theory of the saturation capacity of these atoms. This is the theory of valence or quantivalence or atomicity, and without it the equivalents are purely empirical, and it is most difficult if not impossible to clear up the confusion connected with their use.

Returning now to the derivation of this idea of valence from the type theory, according to Wurtz¹ the conception of valence was introduced into the science in three steps. First there was the discovery of polyatomic compounds. This term was first used by Berzelius in 1827², he applying it to such elements as chlorine or fluorine where he thought several atoms of these elements united with a single atom of another element. The term was later applied by Graham, Williamson, and others to compounds.

The second step was the reference of this polyatomicity to what was called the state of saturation of the radicals contained in these compounds. This was largely through the work of Williamson and Gerhardt.

Thirdly this conception of saturation was extended to the elements themselves. This was chiefly due to the work of Frank-

¹ *Histoire des doctrines chimiques*, p. 69.

² *Jsb. d. Chem.*, 7, 89.

land upon the organo-metallic compounds. And so valence has come to refer to the number of atoms with which a single atom of any element will combine.

This conception has then been one of slow growth, gradually incorporating itself into the science as the necessity arose of devising a suitable explanation for accumulated observations. It was a logical outcome of and was evolved from knowledge acquired step by step. It was no mere speculation or hypothesis, such as that of Prout, evolved by the brilliant fancy or imagination of one man and suddenly appearing with scarcely a claim to foundation upon observed fact.

This conception enters into the chemical theory of to-day almost as fundamentally as the atomic theory itself. Its application is of every-day occurrence and of the most varied character, and yet chemists admit that the nature of valence is one of their chief puzzles and they have advanced but little towards its solution during the past half century. It is quite possible that the ideas to be advanced in the further discussion of this subject in this paper will meet with antagonism. Certainly they should be fully and freely discussed if they are worthy of it. I believe that they form a step toward the clearing up of the mystery of valence.

It is necessary, however, first to trace somewhat further the development of the original conception. One of its earliest and most important applications was to the study of the constitution of the compounds of carbon. Here Kekulé assumed for carbon a constant valence of four, and this idea is still dominant in theories relating to the constitution of these bodies. It was quite natural then that the first belief should have been in a constant valence. It was speedily found, however, that in certain cases, as in the compounds of nitrogen and phosphorus, this belief was scarcely tenable. There were efforts at making it hold good, as, for instance, a distinction was drawn between atomic and molecular compounds, but all of these suggestions have been proved unsatisfactory.

We unquestionably have to account for the existence of a compound with three atoms and another with five atoms in the cases of nitrogen and phosphorus and there are many similar anomalies. Here the valence seems to vary toward one and the same

element. Cases might be multiplied to show also that it varies often towards different elements. Thus it frequently happens that the valence of an element towards hydrogen seems to be quite different from that exhibited toward oxygen. For a long time there was much straining to consider the valence of an element always the same but this effort is, in large measure, abandoned now as unavailing and chemists admit that valence is not constant but variable and may even vary towards one and the same element.

The doctrine of valence has had much added to it about bonds, affinities, and linkage, the necessity for which one may well question. Certainly the misuse of the word affinity here, seeing its other and greater use, should be earnestly discountenanced. I am inclined to think that the other terms bring in false and misleading ideas which should be carefully guarded against. At any rate all hypothetical talk about strong bonds, and weak bonds, double bonds and triple is to be avoided.

If then valence varies, can it be an inherent property of the unchanging atoms? Experiments have shown that it varies with the nature of the combining element, that it varies with the temperature and with other conditions. It is not dependent upon the atomic weight in the same sense as other properties are dependent upon it. Thus in the same group the valence remains the same whether the atoms weigh nine times as much as hydrogen or two hundred times as much.

We seem shut up to the conclusion that valence is not one of the primitive inherent properties of the atom but is relative. It is rather to be regarded as the resultant of the mutual influence of the atoms of the combining elements. The clear grasping of this idea is an important step forward. Unfortunately the distinction is not always made nor consistently adhered to.

It may not be amiss to cite here the utterances of Lothar Meyer in regard to the question of a constant or variable valence.¹

“Since the aim of all scientific investigation is to exhibit the most variable phenomena as dependent upon certain active invariable factors taking part in them and in such a manner that each phenomenon appears to be the necessary result of the properties and reciprocal action of these factors, then it is clear that

¹ Modern Theories of Chemistry, Eng. Trans., p. 303.

chemical investigation would be considerably advanced were it possible to prove that the composition of chemical compounds is essentially determined by the valency of the atoms and the external conditions under which these atoms react upon one another. The first necessary step in this direction has been made in the attempt to explain the regularities observed in the composition of chemical compounds, by the assumption of a constant power of saturation or an invariable valency of the atom. The opposite and equally hypothetical assumption that the valency is variable leads to no advancement.

“The first step towards progress in this matter would be made if some hypothesis as to the cause of this variability were proposed. This difference between the two attitudes has seldom been properly realized. While some chemists, accepting the the constant valency of atoms, have attempted to deduce the varying atomic linking from one distinct point of view, others have considered it sufficient to have assigned to the atom of a particular element in one compound one valency, and in another compound a different valency, according as this or that value appeared the most suitable, and thus to have given a so-called explanation of the composition of the compounds in question. In this way the fact has been overlooked, that an arbitrary interpretation carried out by means of chosen hypotheses, cannot be regarded as an attempt at a scientific explanation, but is nothing more than an expression of our ignorance of the causal connection of the phenomena. An explanation would require that the different valencies assigned to one and the same element in different compounds, should be traced to a distinct cause. If, for instance, it is stated that carbon in carbon dioxide possesses double the valency which it possesses in carbon monoxide, such a statement is no explanation of the fact that an atom of carbon in the former compound is combined with twice as much oxygen as in the latter, for such a statement is merely a paraphrase which hides its incompetency by assuming the form of an explanation. Although this may be perceived without further remark, still it has frequently occurred during the past few years that similar paraphrases have not only been proposed but also accepted as real explanations of such phenomena. Just as it was formerly supposed that the assumption of a vital force dis-

pensed with a more complete investigation of the phenomena of animal life, so many chemists have of late thought that they possessed in 'variable valency', a means of explaining the varying stoichiometric relationships which would satisfy all claims. Such deceptions can only retard the advance of the science, since they prevent an earnest and thorough investigation of the question, whether each atom is endowed with a property determining and limiting the number of atoms with which it can combine, dependent upon the intrinsic nature of the atom and like it invariable; or whether this ability is variable and with it the nature of the atom itself."

It is not strange that this line of reasoning should lead Lothar Meyer to doubt the unvarying nature of the atom itself, and thus losing his grasp upon one invariable to make sure of another. He says: "It is by no means impossible that the magnitudes which we now style atoms, may be variable in their nature."

It will be an unfortunate day for chemists when the belief in the unchanging atom is given up. Chaos will indeed enter into all of our theories when this, the foundation rock, is left at the mercy of every shifting tide of opinion and can be shaken by all manner of unfounded hypotheses.

The case cannot be so hopeless as to necessitate calling to our aid so dangerous a doctrine. Before turning to such an expedient let us first make all possible use of our atomic theory as it stands. The extension of this theory teaches that the atoms are endowed with motion and this motion probably varies in velocity and phases with the different elements. So too when the atoms unite the resulting molecule has a certain motion peculiar to it while the atoms composing it have an intra-molecular motion in which their original motions are probably modified by their influence upon one another. It is quite manifest then that a molecule, in order to exist, must maintain a certain equilibrium and harmony between these various motions, and that there can be all degrees of equilibrium from the very stable to that which may be upset by the least disturbing influence from without.

It seems to me that herein we have a full and satisfactory means of explaining the various problems connected with the conception of valence. The question as to whether the atoms of two elements will unite is decided by affinity, which is in some

way connected with the electrical condition of those atoms. There is no apparent connection between this and valence. The number of atoms which enter into combination forming one molecule is purely a matter of equilibrium and is dependent upon the motion of those atoms. Thus a phosphorus atom unites with chlorine atoms because of a certain affinity between them. The number of chlorine atoms with which it will unite depends upon the possibility of harmonizing the respective motions. As the temperature may affect these motions and also impart a more rapid molecular motion, it is evident that the harmony, or equilibrium, will depend upon the temperature and that a temperature may be reached at which no harmony is possible and hence no compound can be formed. The phosphorus atom mentioned can, as we know, form a stable molecule with five atoms of chlorine. On increasing the temperature this becomes unstable and only three atoms can be retained. Neither with four atoms nor with two is there harmony of motion. A sufficiently high temperature may prevent any harmony of motion whatever being attained and hence union may become impossible.

As to other influences than those of temperature, we can see that the equilibrium between the atom of phosphorus and the five atoms of chlorine may be upset by such a molecule coming within the influence, electrical or vibratory, of a molecule of water. The atoms must rearrange themselves for a new state of equilibrium and so an atom of oxygen takes the place of two atoms of chlorine, giving again a condition of harmony. In other cases the motion of the molecule of water may be of such a character as to directly harmonize with that of the original molecule and so to enter into equilibrium with it, a definite number of such molecules of water affording a condition of maximum stability. This we call water of crystallization. Such molecules would be more or less easily separated by an increase of temperature and where several molecules of water were attached the highest temperature would be necessary for freeing the original molecule from the last water molecule.

A carbon atom finds its most perfect state of equilibrium where four atoms of hydrogen or their equivalents move in harmony with it. But there is a second state of equilibrium where only

half that number of atoms are moving with it. This state does not seem to be a possibility where these are hydrogen atoms but is readily possible where the equivalent number of oxygen atoms is concerned. Such a molecule, however, is always in a condition to take up additional atoms until its highest equilibrium is reached and in doing this it proceeds by the regular steps needed for bringing about a harmony of motion. A molecule in a lower state of equilibrium we have become accustomed to call unsaturated, calling that one saturated which is in its highest state of equilibrium. The further application of this hypothesis is easily made and need not be dwelt upon here. It will be helpful in many ways.

This theory of valence makes it clear why it should vary toward the same element under different conditions. It is also clear that it might vary towards different elements as these are very possibly possessed of different motions. It is further evident that it is in accord with the conclusion that valence is not an inherent property of the individual atom but is the resultant of the influence upon each other of the combining atoms.

Only one point remains to be considered: Why do the elements of the same group have practically the same valence? The nearest answer to this, and it seems satisfactory, is that they are all possessed of the same phase or kind of motion. In other words the natural division into periods gives us seven or eight more or less different phases. These are, in large measure, independent of the atomic weight. And so the elements in any given group have the same tendency towards similar states of equilibrium in forming compounds with any other element, as hydrogen or oxygen. Some elements, as copper, mercury, tin, etc., are peculiar in that they may change their phase of motion under certain influences, acting then as if they belonged to different groups and entering into totally different states of equilibrium in forming their compounds.

Lastly it is possible for a combination of atoms of different elements, as NH_4 or CN , to have such molecular and intra-molecular motion that, although not in a state of equilibrium themselves, they are capable of entering into such states just as the single atoms of elements do, having apparently similar valence.

I might develop this theory much further but it is unnecessary

now. Enough has been said to show that such an application of the atomic theory is legitimate and is most highly important as a step towards the clearing up of the problems springing from the conception of valence and from the periodic system.

Note.—Since certain points in this paper require treatment at greater length than was practicable in an address, it will be followed by a second paper elaborating such portions.

UNIVERSITY OF NORTH CAROLINA, December 29, 1898.

SIXTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED IN 1898.

BY F. W. CLARKE.

Received January 10, 1898.

DURING the year 1898, there has been an increased activity in the determination of atomic weights, and a considerable number of investigations have been published. The importance of the subject is also indicated by the fact that the German Chemical Society has appointed a strong committee to report annually upon atomic weights; and its action for the current year is stated farther on. The new data are as follows:

OXYGEN.

Keiser¹ has effected the complete synthesis of water, by a new method, in which the hydrogen held by palladium, the oxygen, and the water produced are all determined by successive weighings in one and the same apparatus. For details of construction, etc., the original memoir must be consulted. The data for four experiments are as follows:

Weight H.	Weight O.	Sum H + O.	Weight H ₂ O.
0.27549	2.18249	2.45798	2.45975
0.27936	2.21896	2.49832	2.49923
0.27091	2.15077	2.42168	2.42355
0.26845	2.13270	2.40115	2.40269

From columns first and second, the ratio H : O can be computed, while the first and fourth give the ratio H : H₂O.

Ratio H : O.	Ratio H : H ₂ O.
7.922	8.929
7.943	8.946
7.939	8.946
7.944	8.950
<u>Mean, 7.937</u>	<u>Mean, 8.943</u>

From ratio H : O, O = 15.874
 " " H : H₂O, O = 15.886

Mean, 15.880

¹ *Am. Chem. J.*, 20, 733, November, 1898.