

# SCIENCE

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TYPES OF VALENCE

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FROM the theory proposed by G. N. Lewis in 1916 and subsequently extended by the writer, it is clear<sup>1</sup> that the term valence has been used in the past to cover what we may now recognize as three distinct types of valence, viz.:

1. Positive valence: the number of electrons an atom can give up.
2. Negative valence: the number of electrons an atom can take up.
3. Covalence: the number of pairs of electrons an atom can share with its neighbors.

It was shown that these fundamental conceptions of valence as well as the actual numerical values of each type of valence for most of the elements could be derived from a few postulates regarding the structure of atoms. The following method of deriving these relationships, however, is not only much simpler than that previously given by the writer, but throws a new light on the relationships between the different types of valence.

We will take for granted the Rutherford type of atom, which consists of a positive nucleus surrounded by a number of electrons equal to the atomic number of the atom. We will also assume that Coulomb's law applies to the forces between the charged particles in the atom, but at the same time will recognize the existence of repulsive forces in atoms which prevent the electrons from falling into the nucleus. For the present purpose, however, it is immaterial whether the repulsive force is a dynamic force (centrifugal force) such as that assumed by Bohr, or is a static force as postulated by G. N. Lewis, J. J. Thomson or recently by the writer.<sup>2</sup>

We shall need to make only 3 postulates in

<sup>1</sup> Langmuir, *Jour. Amer. Chem. Soc.*, 41, 926 (1919), and *Jour. Ind. Eng. Chem.*, 12, 386 (1920).

<sup>2</sup> SCIENCE, 53, 290, Mar. 25, 1921.

regard to the structure of atoms, and these are consistent with those previously proposed.

*Postulate 1.*—*The electrons in atoms tend to surround the nucleus in successive layers containing 2, 8, 8, 18, 18 and 32 electrons respectively.*

The word atom is used in the broader sense which includes charged atoms (ions). If the number of electrons in an atom is such that they can not all form into *complete layers* in accord with Postulate 1, the extra electrons remain in the outside layer as an *incomplete layer* which we may designate as the *sheath* of the atom. Every electrically neutral atom must contain a number of electrons equal to the atomic number of the nucleus. If the outside layer of such an atom is nearly complete, the tendency expressed by Postulate 1 may cause a few additional electrons to be taken up in order to complete the layer, thus forming a negatively charged atom or ion. In such a case we may say that the sheath has been completed.

In the following discussion it is important to keep in mind this distinction between sheath and outside layer. Every incomplete outside layer which occurs normally is a sheath, but a complete outside layer may or may not be a sheath. The following definition will make this clearer. *The sheath of any atom (or atomic ion) consists of all the electrons in the outside layer provided that this layer is incomplete when the atom is electrically neutral.* Thus atoms of the inert gases (neon, argon, etc.) and ions such as  $\text{Na}^+$ ,  $\text{Ca}^{++}$ , etc., have *no sheaths* for the outside layers of these atoms consist of electrons which already form a complete layer in the neutral atom. The sodium atom, however, has an *incomplete sheath containing* one electron, while the fluorine atom has an incomplete sheath of 7 electrons. The fluorine ion, on the other hand, has a *complete sheath* of 8 electrons.

The inert gases are the only elements whose neutral atoms have no sheaths, or in other words have all their electrons arranged in complete layers in accordance with Postulate 1. In all other atoms, the tendency expressed by

this postulate can only be satisfied by an interaction between atoms involving a rearrangement of the electrons. This is to be regarded as the fundamental cause of chemical action and it is by such interaction that chemical compounds are formed.

When as the result of such rearrangement of electrons, the sheath of an atom has become complete, we may speak of the atom as a *complete atom*. Similarly if the interaction between atoms leads to complete satisfaction of the tendency of Postulate 1, so that all the atoms become complete, we may say that a *complete compound* is formed. We shall see that there are some factors which may oppose the formation of complete atoms and counteract the tendency of Postulate 1. In such cases incomplete atoms and compounds may result.

According to Postulate 1, the first complete layer in any atom consists of two electrons close to the nucleus. Let us call this stable pair of electrons a *duplet* and let us broaden the definition of duplet to include any pair of electrons which is rendered stable by its proximity to one or more positive charges. We may now state the second postulate.

*Postulate 2.*—*Two atoms may be coupled together by one or more duplets held in common by the completed sheaths of the atoms.*

Let us now analyze the conditions that must be fulfilled if the interaction between atoms is to result in the formation of a complete compound.

A given group of neutral atoms may interact to complete their sheaths in two ways:

1. *By transfer of electrons.*
  - a. Atoms having sheaths containing only a few electrons may give up these extra electrons to other atoms.
  - b. Atoms having nearly complete sheaths may take up electrons from other atoms.
2. *By sharing duplets.*

Atoms may share duplets with other atoms (Postulate 2) and thus complete their sheaths with fewer elec-

trons than would otherwise be necessary.

Let  $e$  be the number of electrons in the sheath of any neutral atom and let  $s$  be the number of electrons in the sheath after the atom has interacted with others. For the atoms of any complete compound the values of  $s$  can be only 0, 2, 8, 18 or 32.

In any group of atoms, the only electrons available for the formation of the complete sheaths are those which originally form the incomplete sheaths. The number of such electrons,  $\Sigma(e)$ , is found by adding the values of  $e$  for the individual atoms. In the resulting compound, if no duplets are shared by the atoms, the total number of electrons in the complete sheaths is  $\Sigma(s)$ . Every duplet held in common by two atoms, however, decreases by two the number of electrons required to form the sheaths. If then we let  $B$  be the total number of duplets shared within the given group of atoms, the number of electrons in the completed sheaths of the atoms of the compound is  $\Sigma(s) - 2B$ . Since this must equal the number in the original neutral atoms, we have the relation<sup>3</sup>

$$\Sigma(e) = \Sigma(s) - 2B. \quad (1)$$

This is the condition for the formation of a complete compound. We shall now proceed to put this equation into a simpler form and one which has more significance to the chemist.

The transfer of electrons that may occur during the interaction between atoms corresponds to what has been called positive and negative valence while the sharing of duplets corresponds to covalence. We shall see that the positive and negative valence differ from one another fundamentally only in algebraic sign, so that we shall find it convenient to include both positive and negative valence under the term *electrovalence*, which we may designate by the symbol  $v_e$ . We shall then adopt the convention that the electrovalence

<sup>3</sup> Equation (1) is a more general statement of the relation  $e = 8n - 2p$  which has been used previously by the writer in discussing the "octet theory."

of an atom is positive when the atom gives up electrons and negative when it takes up electrons. The *electrovalence* of an atom in any compound may thus be defined as the number of electrons which the neutral atom must give up in forming that compound. If the neutral atom must *take up* electrons, the electrovalence is expressed as a negative number. The electrovalence of any atom is thus given by the expression

$$v_e = e - s. \quad (2)$$

Electropositive atoms in complete compounds lose all the electrons in their sheaths so that  $s$  is zero and therefore  $v_e$  is positive and equal to  $e$ . For electronegative atoms  $s$  is always greater than  $e$  so that  $v_e$  is negative.

Let us define the *covalence* ( $v_c$ ) of an atom as the number of duplets which that atom shares with neighboring atoms. Every duplet shared by two atoms corresponds to a (covalence) *bond* between atoms, and we have already represented the number of such bonds in a given group of atoms by the symbol  $B$ . If we now form  $\Sigma(v_c)$  by adding the values of  $v_c$  for all the atoms in the given group, we count each bond twice. Hence we may place

$$\Sigma v_c = 2B. \quad (3)$$

By substituting (3) and (2) in (1) and rearranging terms we find

$$\Sigma v_e + \Sigma v_c = 0. \quad (4)$$

This simple result may be stated as follows:

*The sum of the electrovalences and covalences for all the atoms in any complete compound is zero.*

Electrovalence and covalence are thus in a sense supplementary to one another. If we represent  $v_e + v_c$  by  $v$ , Equation 4 takes the form

$$\Sigma v = 0 \quad (5)$$

for any complete compound, and this suggests that the quantity  $v$  may have some simple physical significance.

In accordance with the nomenclature introduced by Lewis we may define the *kernel* of an atom as that part of an atom which re-

mains after the sheath is removed. Since the neon atom has no sheath the whole atom constitutes a kernel with zero charge. The kernel of the sodium atom is the sodium ion with single positive charge, while the kernel of the fluorine atom (or fluorine ion) consists of the nucleus and two electrons, the whole having 7 positive charges.

Since the sheath of any neutral atom consists of  $e$  electrons, the positive charge on the kernel is also  $e$ . In any complete atom there are  $s$  electrons in the sheath. When the atom does not share duplets with other atoms (covalence zero) then the total charge of the atom is  $e - s$ . If, however, any two atoms hold a duplet in common the total charge of the two atoms is decreased by two units. *If the two atoms are substantially alike in size and structure*, we may assume that this decrease in charge is to be divided equally between the two atoms. Thus if an atom in a compound has  $s$  electrons in its sheath and it has a covalence  $v_c$ , then the effective charge of its sheath is  $s - v_c$ . The total charge of the atom may thus be taken as

$$e - (s - v_c) = v_e + v_c = v.$$

Thus  $v$ , the sum of the electrovalence and the covalence, for any atom in a compound, is equal to the *residual atomic charge*.

When two atoms which hold a duplet in common differ considerably in size, it is no longer obvious that the two electrons of the duplet should be divided equally between the two atoms in determining the residual charge. We may, however, arbitrarily so define the boundaries of the individual atoms in molecules that a duplet binding two atoms together is to be regarded as belonging equally to the two atoms. In this case we may consider  $v$  to be the residual atomic charge even when the atoms differ greatly in size.

It is evident from Coulomb's law that the separation of positive from negative charges requires in general the expenditure of work. The most stable forms of matter should be those in which the positive and negative charges are as near together as possible. However, we can not rely entirely upon Coulomb's

law for this would indicate that the distance between unlike particles should decrease without limit. The exact distribution of charged particles in their most stable arrangement thus requires a knowledge of the repulsive forces whose existence we have already assumed. A further discussion of this point will be reserved for a future paper. At present we may attempt to express this relation by the following postulate.

*Postulate 3.—The residual charge on each atom and on each group of atoms tends to a minimum.*

By "residual charge" is meant the total charge of an atom or group of atoms regardless of sign. By "group of atoms" is meant any aggregate of atoms which are characterized by proximity to one another. It is felt by the writer that this postulate is a crude expression of a very important and fundamental law. When we understand the repulsive forces between charged particles better we shall be able to state the law in a more nearly quantitative form. The law is of very wide application. The uniformity of distribution of positive and negative ions in a salt solution is a familiar example of the working of this law. In any small finite element of volume the charges of the positive and negative ions tend to be very nearly equal or the residual charge tends to a minimum.

Postulate 3 expresses merely a strong *tendency* so that in general the charges of individual atoms are not necessarily zero. When the atomic charges depart from zero, however, they do so only as the result of a definite force or action which opposes the tendency of Postulate 3. We shall see that Postulates 1 and 3 are often in conflict and in such cases the tendency of Postulate 1 may prevail against that of Postulate 3.

We may now classify chemical compounds according to the types of valence exhibited by their atoms and will consider the application of Postulate 3 to each class of compound. There are 3 general subdivisions to consider:

(1) Complete Compounds, (2) Incomplete Compounds, and (3) Exceptional Cases.

1. COMPLETE COMPOUNDS.—All electrons are

in complete layers of 2, 8, 18 and 32 electrons, in accordance with Postulate 1. Since  $\Sigma v_e$  in Equation 4 can never be negative,  $\Sigma v_e$  must always be either zero or negative. Therefore atoms having negative valences must always be present in a complete compound. Thus electropositive elements do not form complete compounds with each other.

*a. Compounds Without Covalence.*— $\Sigma v_e = 0$ . Equation 4 becomes  $\Sigma v_e = 0$ , so that the sum of the negative valences in the compound must be the same as the sum of the positive valences. Since the residual charge  $v$  for each atom must equal  $v_e + v_c$  it is evident that compounds without covalence must consist of positively and negatively charged ions. The charge  $v$  on each ion of complete compounds of this type is uniquely determined by the values of  $e$  for the elements forming the ion. This is a case where Postulates 1 and 3 are in conflict. The tendency of Postulate 3 by itself would make each atom electrically neutral, but this would leave the sheaths of the atoms incomplete and so fail to satisfy the tendency of Postulate 1. The result is a kind of compromise by which Postulate 1 may be satisfied by the formation of complete compounds *provided this can take place without the charges on the ions becoming too large*.

Although Postulate 3 does not definitely fix the charges of the individual atoms in the compounds we are considering, yet it does determine the distribution of these ions in space. This is a factor of prime importance in the crystal structure, in the electrolytic conductivity of substances when in the liquid state, and in other properties. It is also the cause of an interesting effect observed when the number of ions of one sign is much greater than that of the other sign, as for example in such compounds as  $\text{AlCl}_3$ ,  $\text{PCl}_5$ ,  $\text{SF}_6$ , etc. Postulate 3 requires that the negative halogen atoms in these compounds shall surround the most strongly positive atoms. The ions thus form groups having strong internal and weak external fields of force so that these constitute molecules of considerable stability and inertness towards outside influences. The

volatility of these substances and the absence of electrolytic conductivity are due to this cause.

Typical examples of complete compounds without covalence are:

*Salts.*—When the atomic charges are small as in  $\text{NaCl}$ ,  $\text{BaBr}_2$ ,  $\text{K}_2\text{S}$ , etc., the salts are fairly readily fusible, soluble in liquids of high dielectric constant, good electrolytic conductors when molten or in solution and very difficultly volatile. With larger charges as in  $\text{MgO}$ ,  $\text{BN}$ ,  $\text{Al}_2\text{O}_3$ , etc., the strong forces give great infusibility, insolubility, hardness, etc., to the substance. Such compounds are exceptionally good electric insulators at moderate temperatures but are electrolytic conductors when molten.

*Silicates, glasses, slags, complex sulfides, and most minerals, etc.*, are compounds which usually contain several electropositive elements. In the molten, and often in the solid condition, they are electrolytic conductors and are usually soluble in one another. The valence relation  $\Sigma v_e = 0$  gives us no information in regard to the structure; for example, we can not write structural formulas for such compounds. The definite composition of many solid minerals, etc., is largely due to the regularities of the space lattices of their crystals.

*Volatile halogen compounds* such as  $\text{AlF}_3$ ,  $\text{PCl}_5$ ,  $\text{SF}_6$ , and structurally related complex ions such as  $\text{SiF}_6^{--}$  in the compound  $\text{K}_2\text{SiF}_6$ . Such high electrovalences as +5 for phosphorus, and +6 for sulfur can occur only when the tendency of Postulate 3 is counteracted by a particularly strong opposing tendency. In the case cited above it is the exceptionally great affinity of the halogen atoms for electrons that causes the action. The halogen atoms have this property in marked degree because they have larger charges on their kernels than other atoms and therefore exert a greater attraction on electrons (Coulomb's law). The fluorine atom has a greater affinity for electrons than the other halogen atoms since the radius of the atom is less and the force (by Coulomb's law) acting on the electron is greater.

*b. Compounds Without Electropositive*

*Atoms.*—In these compounds the electrovalence of every atom must be negative, for if the electrovalence of any element is zero (inert gases) it can form no compounds. If we let  $v_n$  represent the numerical value of the negative valence we obtain from Equation 4

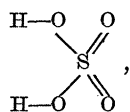
$$\Sigma v_c = \Sigma v_n. \quad (6)$$

Since  $v_n = s - e$ , the value of  $v_n$  is fixed for any particular atom. For any given group of atoms, we can find  $\Sigma v_c$  from (6) but we can not find the values of  $v_c$  for the individual atoms, in this way.

If, however, we place  $v_c = v_n$  for each atom it is evident that Equation 6 will be satisfied. The residual charge on every atom (being  $-v_n + v_c$ ) is then zero. Thus in any group of atoms *Postulates 1 and 3 are both completely satisfied if the covalence of each atom is equal to the negative valence of that atom.* The negative valence of carbon, nitrogen, oxygen and sulfur are 4, 3, 2 and 2 respectively, while that of hydrogen and the halogens is one. If therefore we follow the custom of the organic chemist and write structural formulas using these valences we obtain results in complete accord with Postulates 1, 2 and 3.

Thus these 3 postulates lead us to a rational derivation of the empirical valence rules which constitute the foundation of the science of organic chemistry. Moreover we are brought to see clearly the limitations of this empirical theory. We now realize that it is only *negative* valences that should be used in structural formulas (*i.e.*, as covalences) and that even these can only legitimately be used in compounds in which electropositive atoms are entirely absent, for if some of the atoms have a positive residual charge ( $v = v_c$ ) then from Eq. 5 it is evident that other atoms must have a negative charge, and for these as well as the electropositive atoms the covalence is not equal to the negative valence.

From this viewpoint it is incorrect to write structural formulas such as Na—Cl,



etc., in which the covalence of one atom is taken as equal to the positive valence of that atom.

It should be kept in mind that Postulate 3 does *not require* that  $v_c$  should be equal to  $v_n$ . There is merely a tendency for these valences to be equal. Among compounds of electropositive elements we saw that there was a conflict between the tendencies of Postulates 1 and 3 so that  $v$  was always different from zero. With compounds formed exclusively of electro-negative atoms, however, there is not necessarily a conflict and it is for this reason that we have such a large class of compounds in which  $v$  is zero (*i.e.*,  $v_c = v_n$ ). There may be various causes that make it difficult for  $v$  to be zero even for some compounds of electro-negative elements, so that in individual cases  $v$  may differ from zero by one or two units. It must be remembered that we deduced the relation  $v = \text{minimum}$  from Postulate 3 only by assuming the two atoms which share a duplet are of substantially the same size, etc. From Coulomb's law we should expect that either a large charge on the kernel of an atom or a small radius for the kernel should cause electrons in the sheath to be held more firmly and should make it easier for the atom to acquire a negative residual charge. As an example let us consider the electronegative elements of the first two periods.

As we pass from carbon, through nitrogen and oxygen, to fluorine, the kernel charge increases and the size of the kernel presumably decreases. The residual atomic charge should thus tend to become more negative as we pass towards fluorine and more positive in comparison as we pass towards carbon. In other words, in compounds of these elements, we should expect a tendency for fluorine to have a covalence a little less than its negative valence while for nitrogen the covalence should tend to be greater than the negative valence. Since there are only eight electrons in the sheath of these atoms, the covalence of the carbon atom can never exceed four. All these conclusions are in perfect accord with experience. Thus we find the following covalences:<sup>4</sup>

Carbon .....	4	(3)				
Nitrogen .....	4	3	(2)			
Oxygen .....	(3)	2		1	0	
Fluorine .....				1	0	
Silicon .....	4	(or electro-positive)				
Phosphorus .....	4	3				
Sulfur .....	4	3	2	1	0	
Chlorine .....	(4)	(3)	(2)	1	0	

In this table the numbers in italics give the most common valences, while those in parentheses are only rarely found. It is clear that a large kernel charge favors covalences less than the negative valences while a small kernel charge has the opposite effect. A comparison of the elements of the second period with those of the first, shows a slight tendency for larger covalences among the heavier elements. This is to be explained as the effect of the larger kernel and hence weaker forces. There is also much more scattering among the valences of the heavier elements. This is another result of the weaker forces acting on the electrons for the covalence of such atoms is more dependent upon the electron affinity of the other atoms with which they are combined.

As an example of these relationships, let us consider the compounds,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$ . In each atom of these compounds the covalence is equal to the negative valence so that the residual charge is zero and the tendencies of Postulates 1 and 3 are satisfied. If we mix the  $\text{NH}_3$  and  $\text{HF}$  together the larger kernel charge of the fluorine as compared with the nitrogen, gives a tendency for the fluorine atom to become negative at the expense of the nitrogen. Thus the covalence of the fluorine decreases to zero while that of the nitrogen increases to four. This leads to the formation of the compound  $\text{NH}_4\text{F}$  which consists of  $\text{NH}_4^+$  ions and  $\text{F}^-$  ions. The total number of covalence bonds has not been changed, they have merely been distributed differently. But this causes the atoms to become charged and makes the compound an electrolyte. It should be noted that this theory indicates definitely in what direction the change of charge occurs. Thus we should not

<sup>4</sup> See Langmuir, *Jour. Amer. Chem. Soc.*, 41, 927 (1919).

expect  $\text{NH}_3$  and  $\text{HF}$  to give a compound consisting of ions  $\text{NH}_2^-$  and  $\text{H}_2\text{F}^+$  although under other conditions these ions might exist.

Similarly  $\text{NH}_3$  and  $\text{H}_2\text{O}$  may react to form  $\text{NH}_4\text{OH}$  which will consist of ions  $\text{NH}_4^+$  and  $\text{OH}^-$ . But the tendency to form a compound such as this is much less than in the case we have just considered, for the charge on the kernel of the oxygen atom is less than that of the fluorine atom so it has less tendency to become negative. As a result  $\text{NH}_3$  is much less active towards  $\text{H}_2\text{O}$  than towards  $\text{HF}$ . Examples of this kind can be extended almost indefinitely and can even be used to obtain quantitative relationships between the heats of formation of various substances.

Since the sheaths of atoms of atomic number less than about 25 never contain more than 8 electrons, the covalence of these atoms can not exceed 4. With heavier atoms, however, we might expect in some cases larger covalences than 4. Large covalences are improbable in most cases for they imply equally large negative valences which means that the number of electrons in the sheath must be very much larger than the charge of the kernel. There are a few compounds, however, which suggest that large covalences sometimes exist. For example the compounds  $\text{Fe}(\text{CO})_5$  and  $\text{Ni}(\text{CO})_4$  correspond to complete compounds in which the central atoms have the covalences 10 and 8 respectively. Since  $e$  for iron is 8 and for nickel is 10 and the complete sheaths for these atoms contain 18 electrons, the negative valences of iron and nickel are 10 and 8, that is the same as the covalences needed to account for the above compounds. Thus these compounds are in accord with both Postulates 1 and 3, and are to be regarded as of a type analogous to organic compounds in which the covalence of every atom is equal to its negative valence. It should be noted that both of these compounds are liquids of low boiling point ( $102^\circ$  and  $43^\circ$ ) and their molecular weights have been determined. Their properties are about those to be expected if they have the structure assumed above. Other compounds of iron with carbon monoxide are known, but they have only been obtained in

the crystalline state and their molecular weights are unknown.

Molybdenum carbonyl,  $\text{Mo}(\text{CO})_6$ ,<sup>5</sup> is a very easily *volatile* crystalline compound. It is interesting to note that the *negative valence* of molybdenum ( $s - e = 18 - 6$ ) is twelve, so that with a covalence of 12 for the molybdenum atom in this compound we again obtain a structure consistent with the valence theory discussed above.

2. INCOMPLETE COMPOUNDS.—These are compounds in which some of the electrons are not arranged in complete layers or sheaths, so that the tendency of Postulate 1 is not completely satisfied. This can only occur as a result of a conflict between Postulate 1 and Coulomb's law or Postulate 3. We have seen that the tendency of Postulate 3 causes the residual charge ( $v$ ) on each atom to be a minimum. The tendency of Postulate 1, however, is sufficiently strong to force the atoms to take up charges of 3, 4, or even under some conditions, 5 or 6 units, if this should be necessary in order to bring all the electrons into complete layers. Since there must be a limit to the strength of the tendency of Postulate 1 it is not surprising that residual atomic charges greater than 4 or 6 are very rare. Now the atoms of the elements near the middles of the long periods (of 18 and 32 elements), do not become complete even if they do acquire residual charges as great as 5 or 6 units, and it is therefore natural that the tendency of Postulate 3, which must become stronger as the charge increases, should prevent the formation of complete compounds of these elements. There are two types of incomplete compounds to consider.

*a. Metallic Substances. Electronegative Atoms Absent.*—By Coulomb's law, atoms having only small charges on their kernels, should not be able to take up enough electrons to complete sheaths of 8 or more electrons. Thus if we bring together a number of electropositive atoms there is no way in which the electrons in the incomplete sheaths can rearrange themselves to form complete sheaths. The

<sup>5</sup> Mond, Hirtz, Cowap, *J. Chem. Soc.*, 97, 798 (1910).

“free” electrons which are thus compelled to remain in incomplete sheaths are responsible for the metallic properties shown by all electropositive elements in the solid or liquid state. It is clear, however, notwithstanding the fact that hydrogen may sometimes function as an electropositive element, that liquid or solid hydrogen should have none of these metallic properties according to this theory, for the sheath to be formed in this case contains only two electrons. The forces acting between the free electrons and the kernels of the atoms in metallic substances, are of the same order of magnitude as in salts, so that metals have about the same range of vapor pressures, hardness, compressibilities, etc., that are shown by salts.

In general, all atoms must be electropositive unless they can take up enough electrons to complete their sheaths and thus act as electronegative atoms. The tendency of Postulate 3 ordinarily prevents the occurrence of negative valences greater than about 4. In the two short periods eight electrons are needed to form a complete sheath so that the elements with kernel charges greater than about 3 can act as electronegative atoms and therefore do not normally show metallic properties. In the 2 long periods 18 electrons form the complete sheath so that about the first 14 of the elements in each of these periods can usually act only as electropositive elements and they thus have metallic properties, when in the elementary form. For similar reasons all the known elements of the rare earth period (the last two being unknown) have metallic properties.

*b. Compounds Containing Electropositive and Electronegative Atoms.*—As a result of Coulomb's law or Postulate 3, the positive valence of an element is usually limited to a value of 2 or 3 unless particularly strong forces are exerted to draw away electrons, and thus raise the positive valence a few units higher. Thus in the middle of the long periods the charges of the kernels are so great that all the electrons in the sheaths of the electropositive atoms can not be given up even when other atoms are present that can take up electrons. It thus happens that the long pe-



riods contain series of elements which all have 3 or 2 and 3 as their principal valences. The atoms of these elements are therefore incomplete. The electronegative atoms in such compounds, however, are always complete.

It is of interest to note that as long as atoms are incomplete there seems to be no tendency for them to have an even rather than an odd number of electrons. For example, the following ions all have odd numbers of electrons:  $\text{Cr}^{+++}$ ,  $\text{Mn}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Co}^{++}$ , and  $\text{Cu}^{++}$ . This seems to indicate that the remarkable tendency, pointed out by Lewis, for most compounds to contain even numbers of electrons is due merely to the relative abundance of complete compounds as compared to incomplete ones. In other words, the even number of electrons in most compounds results from the tendency of Postulate 1 rather than from any more general tendency for electrons to form pairs.

Many of the compounds of this class, such as  $\text{ZnO}$  (zincite),  $\text{Fe}_3\text{O}_4$ ,  $\text{PbS}$ ,  $\text{CuO}$ , etc., show electric conductivity even as solids. This is undoubtedly caused by the relatively large number of electrons in incomplete sheaths. Of course we should not expect all compounds which contain such electrons to show conductivity, for the presence of the electronegative atoms might easily prevent the mobility of these electrons. We need to know much more than we now do about the arrangement of the atoms and their electrons in space before we can predict conductivity in particular cases of this kind.

3. EXCEPTIONAL CASES.—There are some substances or compounds whose structure is not adequately accounted for by the foregoing analysis. A few examples are:  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{NO}$ . The writer believes these have the single octet structure which he described in his earlier publications. It is probable that acetylene,  $\text{C}_2\text{H}_2$ , and the carbide ion  $\text{C}_2^{--}$  (in  $\text{CaC}_2$ , etc.) have the same kind of structure. Pease has suggested that they may all have a triple bond structure.<sup>6</sup> This question merits careful study.

Another set of compounds that must have  
<sup>6</sup> *Jour. Amer. Chem. Soc.*, 43, 991 (1921).

a special structure are various compounds of boron such as  $\text{B}_2\text{H}_6$ .

Most compounds containing molecules of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , etc., are readily accounted for by Postulate 3 but many of these should be considered by methods somewhat different from those developed here.

In double molecules such as  $\text{H}_4\text{O}_2$  (in ice),  $\text{H}_2\text{F}_2$ , and in compounds such as  $\text{KHF}_2$ , etc., it seems that the hydrogen nuclei instead of forming duplets with electrons in the same atom, form duplets in which the two electrons are in different atoms. The hydrogen nucleus itself thus acts as a bond in such a case. Latimer and Rodebush<sup>7</sup> have made a somewhat similar suggestion in regard to hydrogen nuclei acting as bonds. They consider, however, that the hydrogen nucleus acts on two pairs of electrons: one pair in each of the two atoms. It seems to the writer much more probable that the hydrogen nucleus is no more able to attract four electrons than is the nucleus of other atoms. Since the first layer of electrons in all atoms contains only 2 electrons it seems probable that the hydrogen in this case also holds only two electrons and that these form the definite stable group which we have termed the duplet.

The writer plans to consider the quantitative aspects of these valence theories in subsequent papers. It is aimed to put Postulates 1 and 3 into a form that will permit at least rough calculations of the relative stabilities of various substances as measured, for example, by their heats of formation.

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THE men who gave such distinction to botany in Germany during the latter half of the nineteenth century, have mostly gone, the years since 1914 taking heavy toll of those who were left when war broke out. Among the last of the veterans was Professor Bruchmann

<sup>7</sup> *Jour. Amer. Chem. Soc.*, 42, 1431 (1920).