

ELECTRONIC STRUCTURES OF ATOMS¹

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Although the Lewis theory of valence and atomic structure² has met with remarkable success³ when applied to chemical facts, Lewis was able to apply it in its entirety only to some of the elements, chiefly those of lowest atomic weight, from hydrogen to scandium. Among those of higher atomic weight, although some fitted in perfectly with the system, others did not, and it was evident that in order to include all, the theory must be modified or extended in some way.

Langmuir⁴ has attempted to do this, but he was forced to leave still unexplained many valence relationships and other physical and chemical facts. In this and following papers, the author attacks the problem.

The Lewis Theory

Lewis' main assumptions are the following:

1. An uncombined neutral atom has in its outermost shell a number of electrons corresponding to the column of the Periodic Table in which that element belongs.
2. A single bond consists of a pair of electrons holding two atoms together; in a double bond two pairs of electrons join two atoms; and in a triple bond two atoms are connected by three electron pairs.
3. Each atom tends to obtain an even number of electrons in its outer shell, and also to complete its group of eight electrons, or "octet," by bonding with other atoms or otherwise.

¹ This paper, except for minor changes, was written in 1920, but unavoidable circumstances have delayed its publication. A short outline of the theory has recently been published in *Science*, **55**, 459 (1922).

² G. N. Lewis: *Jour. Am. Chem. Soc.*, **38**, 762 (1916).

³ Cf. for example, I. Langmuir: *Ibid.*, **41**, 868, 1543 (1919); **42**, 274 (1920); Latimer and Rodenbush: *Ibid.*, **42**, 1419 (1920).

⁴ Langmuir: *Ibid.*, **41**, 868 (1919).

"Cubical Atom" Versus "Tetrahedral Atom"

Although in the original development of his theory Lewis considered the valence electrons as being approximately at the corners of a cube, in his paper referred to above he proposed, at least for organic compounds, an arrangement in which each pair of electrons acting as a bond is drawn together and occupies one of the four corners of a tetrahedron, the atomic kernel¹ being the center. That the tetrahedron of pairs is the stable arrangement for the valence shells of all of the lighter electronegative atoms, Lewis has believed for some time, and this view will be adopted in this paper. It might be well to briefly consider some of the arguments in favor of this conception.

The cubical arrangement is quite inadequate for the representation of organic compounds. It not only gives no opportunity for the formation of a triple bond, such as must often be assumed between carbon and carbon, carbon and nitrogen, and nitrogen and nitrogen, but is also incompatible with the well-known principle of free rotation about a single bond, for such free rotation could hardly exist if the electrons composing the bond were widely separated from each other.

Whenever an atom of some other element is attached to one of carbon or of nitrogen, the only logical assumption is that the bond connecting the two is here also a pair of electrons which are quite close together. In such a case it would seem very improbable that two of the eight electrons in the shell of this other atom are close together as in a tetrahedral atom, and the other electrons relatively far apart, spaced according to the cubic arrangement. And in the case of an oxygen atom, for instance, doubly bonded to a carbon or nitrogen atom, is it not much simpler to assume that the four electrons not acting as bonds are also paired off than to give them any other less symmetrical positions?

The fact that an atom (of one of the elements considered

¹ This term, introduced by Lewis, is used to denote everything inside of the valence shell.

by Lewis) with an *odd* number of electrons in its outer shell always shows a great tendency to react with other atoms so as to have an *even* number of valence electrons around it,¹ whereas an atom with an *even* number of valence electrons, even though they are not all acting as bonds, is often quite unreactive, is another very potent argument in favor of the pair, rather than the single electron, being the unit (both of bond electrons and of those which are not acting as bonds) in the outer shells of these atoms.

In order to satisfactorily account for the atomic arrangements which have been found to exist in crystals, it seems to be quite necessary to assume that the valence electrons are drawn together in pairs, usually at the corners of a tetrahedron for the lighter elements. Many of the results obtained with this idea as a basis are given in other papers by the writer.²

The Law of Force between Electrons

This pairing of electrons may be readily accounted for by assuming the proper kind of a law (or laws) of force at small distances, as will be shown by an example in the latter part of this paper. The chief requirement of such a law, for this purpose, is that, *as two electrons approach each other, the repulsion between them reaches a maximum at a distance of the order of magnitude of 1 Å. (1 Ångström unit = 10^{-8} cm), the force then decreasing for a considerable proportion of the remaining distance at least (Fig. 1).* The repulsion may or may not change to an attraction. Any of a number of laws of this type will result in the pairing of electrons in atomic shells when they are drawn in, by the attraction of the nucleus, until somewhat closer together than this distance of maximum repulsion.

A law of this type would similarly result in the formation of groups of three electrons, or triplets, when two pairs, or a pair and a single electron, are forced sufficiently close together. In some atoms, moreover, we might expect two or more electronic

¹ Cf. Lewis' discussion of "odd molecules," loc. cit., p. 770.

² Huggins: Phys. Rev., [2] 19, 346, 354, 363, 369 (1922); Jour. Am. Chem. Soc., Sept. 1922.

arrangements to be stable, differing in the numbers of pairs and triplets in the various shells.

Before proceeding to a more complete discussion of the laws of force at small distances, let us see whether the above assumption leads us to atomic structures which are in conformity with the periodic system and the properties of the elements.

Atomic Structures; Hydrogen to Neon

A hydrogen atom possesses one electron which can pair off with a single electron in the shell of another atom, of hydrogen or of some other element. A helium atom contains two electrons outside of the nucleus. These are drawn in so close to the latter that they cannot act in a bond-forming capacity.

A neutral lithium atom possesses three electrons.¹ These we might expect to be arranged symmetrically around the nucleus, giving a trivalent element; but the fact that lithium is monovalent leads us to infer that two electrons tend to be closer to the nucleus (and so, probably, to each other) than the third. Such an arrangement, as will be shown later, may be accounted for by the type of law of force we have assumed, two of the electrons being pulled in by the nucleus until the distance between them (d, Fig. 2) is somewhat less than the distance of maximum repulsion. Because of this fact these two are forced still closer to each other and to the nucleus (represented by a plus sign in the figure), the third electron being at the same time pushed further away from the nucleus.

Increasing the nuclear charge to four, in beryllium, and five in boron, draws the two electrons which are paired closer to the nucleus (and so closer to each other). In carbon, with a nuclear charge of six, the pair has been pulled in so close that the remaining four electrons arrange themselves in tetrahedral fashion, practically as though the inner pair were a part of the nucleus. This pair then persists as the innermost "shell" in the atoms of all of the heavier elements.

In the nitrogen atom we have a case similar to that in

¹ In the following pages, whenever electrons are mentioned, only those outside of the nucleus are considered.

lithium. Five electrons, if placed as symmetrically as possible around the central unit, would be so close to each other that this arrangement would be unstable, and two of the five would be drawn closer together, and the pair thus formed would at the same time be pulled in closer to the nucleus. The resulting arrangement may be looked on as a somewhat distorted tetrahedron, with a pair of electrons at one corner, a single electron at each of the other three corners, and the nucleus and two electrons near the center.

Three more pairs are formed, in like manner, in the next three elements, oxygen, fluorine, and neon. The last has as its outer shell four pairs of electrons at the corners of a regular tetrahedron.

Sodium to Argon

As the nuclear charge increases, the most stable positions for additional electrons are obviously opposite the centers of the faces of the kernel tetrahedron. Even after the four faces are occupied by single electrons, the repulsions of the pairs in the inner shell for the valence electrons are strong enough to cause the latter to form pairs opposite the tetrahedron faces, except in a few compounds¹ in which the valence electrons are pulled so far away from the kernel that they are more influenced by their own repulsions and by the repulsions between the other atoms than by the arrangement of the kernel pairs.

The argon atom consists of a tetrahedron of pairs outside of another tetrahedron of pairs, with a nucleus and two electrons in the center. If these two tetrahedra are the same size, that is, if the electron-pairs are all equidistant from the atomic center, they form a perfect cube. Whether or not this is the case is yet to be determined; it makes little difference in the present theory.

The structures considered up to this point are almost identical with those assumed by Lewis. The properties of the corresponding elements and their compounds have been shown

¹ E. g., H_2SiF_6 , PCl_5 , SF_6 .

by him and by others to be very strikingly in accord with these structures. It is unnecessary, therefore, to consider them in further detail here.

Potassium to Krypton

As the nuclear charge continues to increase, the atom is able to hold additional electrons. These, when the kernel charge becomes great enough to pull them in close to the next inner shell, tend to arrange themselves opposite the faces of the underlying cube or near-cube.¹ The greater the central charge the closer to the nucleus and to each other both the kernel pairs and the valence electrons are drawn. As soon as the distance between two pairs or between a pair and a single electron becomes sufficiently less than the distance of maximum repulsion, a triplet is formed, one electron dropping in from the valence shell to the kernel cube. This increases the repulsion between groups (in the shell containing the triplet) and they are pushed further apart. Another increase in the charge on the nucleus again draws the electron-pairs and the valence electrons closer, another electron drops in from the valence shell, etc. It is quite conceivable that there might be two or more stable arrangements of electrons around a given atomic nucleus, differing in the number of triplets formed in this way, and so in the number of valence electrons. Certainly external conditions, such as the presence of other atoms which tend to hold electrons in the valence shell, can greatly affect the number of valence electrons which drop in from valence shell to kernel. Hence it is but the logical result of this theory that these elements should exhibit considerable variability of valence.

As the number of triplets increases, the repulsion, acting on the remaining pairs, increases and they are forced further and further away from the nucleus. This results, when the nuclear charge is large enough, in the stability of another

¹ It is important that the reader bear in mind throughout this discussion that a *tetrahedron* has 4 corners and 4 faces, a *cube* has 8 corners and 6 faces, and an *octahedron* has 6 corners and 8 faces.

arrangement—that of an octahedron with a tetrahedron outside of it, the corners of the tetrahedron being opposite four of the eight faces of the octahedron. This may be regarded as being derived from the cube by having two of the original pairs forced out of the inner shell, the remaining six groups (at least four of which must be triplets) rearranging themselves to form the octahedron. The two pairs forced out, together with two others, form the outer tetrahedron.

Before proceeding further, it seems best to present a system which has been worked out by the author for the purpose of affording a means of simply representing the structures of complicated atoms. It may be readily understood by a few examples. Atoms of the elements from helium to fluorine in the Periodic Table will be represented by the formula

$$(+ N)(2 \times 1)(n)$$

where “N” is the nuclear charge or atomic number and “n” is the number of valence electrons—0 for He, 4 for C, 7 for F. Elements from neon to chlorine are similarly

$$(+ N)(2 \times 1)(4 \times 2)(n)$$

in which (4×2) represents four pairs of electrons at the corners of a tetrahedron, and the first of those in the third row,

$$\begin{array}{l} (+ N)(2 \times 1)(4 \times 2)(4 \times 2)(n) \text{ or} \\ (+ N)(2 \times 1)(8 \times 2)(n) \end{array}$$

If the two tetrahedra $(4 \times 2)(4 \times 2)$ have the same dimensions, they together form a cube (8×2) . Although a true cube may actually not be obtained for these elements, as already explained, for the sake of simplicity the latter formula will be used in the remainder of the article.

Table I is a compilation of atomic formulae for the elements in their commonest valences. Table II contains formulae representing various typical or unusual compounds, to many of which reference will be made in the discussion which follows.

Titanium and the elements immediately following it show a variability of valence which can be very satisfactorily explained by assuming a falling in of electrons, one by one,

TABLE I
Atomic Structures of the Elements.

H	(+1)(1)	Mg	(+12)(2×1)(4×2)(2)
He	(+2)(2×1)	Al	(+13)(2×1)(4×2)(3)
Li	(+3)(2×1)(1)	Si	(+14)(2×1)(4×2)(4)
Be	(+4)(2×1)(2)	P	(+15)(2×1)(4×2)(5)
B	(+5)(2×1)(3)	S	(+16)(2×1)(4×2)(6)
C	(+6)(2×1)(4)	Cl	(+17)(2×1)(4×2)(7)
N	(+7)(2×1)(5)	A	(+18)(2×1)(4×2)(4×2)or (+18)(2×1)(8×2)?
O	(+8)(2×1)(6)	K	(+19)(2×1)(8×2)(1)
F	(+9)(2×1)(7)	Ca	(+20)(2×1)(8×2)(2)
Ne	(+10)(2×1)(4×2)	Sc	(+21)(2×1)(8×2)(3)
Na	(+11)(2×1)(4×2)(1)		and
Ti	(+22)(2×1)(8×2)(4) (+22)(2×1)(x×3+y×2)(4-x)		x=1(or 2?); y=8-x
V	(+23)(2×1)(8×2)(5) (+23)(2×1)(x×3+y×2)(5-x)		and
Cr	(+24)(2×1)(8×2)(6) (+24)(2×1)(x×3+y×2)(6-x)		x=1, 2 or 3; y=8-x
Mn	(+25)(2×1)(8×2)(7) (+25)(2×1)(x×3+y×2)(7-x)		and
Fe	(+26)(2×1)(x×3+y×2)(4×2)(4-x) (+26)(2×1)(x×3+y×2)(8-x)		x=1, 3, 4, or 5; y=8-x
Co	(+27)(2×1)(x×3+y×2)(4×2)(5-x) (+27)(2×1)(x×3+y×2)(9-x)		x=2; y=4; and
Ni	(+28)(2×1)(x×3+y×2)(4×2)(6-x) (+28)(2×1)(x×3+y×2)(10-x)?		x=2, 4, 5, or 6; y=8-x
Cu	(+29)(2×1)(x×3+y×2)(4×2)(7-x)		x=3; y=3; and
Zn	(+30)(2×1)(6×3)(4×2)(2)		x=5, 6 or 7; y=8-x
Ga	(+31)(2×1)(6×3)(4×2)(3)		x=2, 3 or 4; y=6-x and
Ge	(+32)(2×1)(6×3)(4×2)(4)		x=6, 7 or 8; y=8-x
As	(+33)(2×1)(6×3)(4×2)(5)		x=5 or 6; y=6-x
Se	(+34)(2×1)(6×3)(4×2)(6)		
Br	(+35)(2×1)(6×3)(4×2)(7)		
Kr	(+36)(2×1)(6×3)(4×2)(4×2) (+36)(2×1)(6×3)(8×2)	or	
Rb	(+37)(2×1)(6×3)(8×2)(1)		
Sr	(+38)(2×1)(6×3)(8×2)(2)		
Y	(+39)(2×1)(6×3)(8×2)(3)		
Zr	(+40)(2×1)(6×3)(8×2)(4) (+40)(2×1)(8×3)(6×2)(2)?		and
Cb	(+41)(2×1)(6×3)(8×2)(5) (+41)(2×1)(8×3)(6×2)(3)?		In ZrH ₂ ?
Mo	(+42)(2×1)(6×3)(8×2)(6) (+42)(2×1)(34+x)(6-x)		and
—	(+43)(2×1)(6×3)(8×2)(7)		In trivalent Cb?
			and
			Structure uncertain. x=1, 2 or 3
			and

Ru	(+43)(2×1)(34+x)(7-x) (+44)(2×1)(6×3)(8×2)(8) (+44)(2×1)(34+x)(8-x)	Structure uncertain In RuO ₄ and Structure uncertain. x=1, 2, 4, 5, or 6
Rh	(45)(2×1)(34+x)(9-x)	Structure uncertain. x=6
Pd	(+46)(2×1)(34+x)(10-x)	Structure uncertain. x=6, 8, or 9?
Ag	(+47)(2×1)(8×3)(6×2)(4×2)(1)	
Cd	(+48)(2×1)(8×3)(6×2)(4×2)(2)	
In	(+49)(2×1)(8×3)(6×2)(4×2)(3) (+49)(2×1)(6×3)(8×2)(6×2)(1)	and
Sn	(+50)(2×1)(8×3)(6×2)(4×2)(4) (+50)(2×1)(6×3)(8×2)(6×2)(2)	and
Sb	(+51)(2×1)(8×3)(6×2)(4×2)(5) (+51)(2×1)(6×3)(8×2)(6×2)(3)	and
Te	(+52)(2×1)(8×3)(6×2)(4×2)(6) (+52)(2×1)(6×3)(8×2)(6×2)(4)	and
I	(+53)(2×1)(8×3)(6×2)(4×2)(7) (+53)(2×1)(6×3)(8×2)(6×2)(5)	and In I ₃ ⁻ , ICl ₃ , etc.
Xe	(+54)(2×1)(8×3)(6×2)(4×2)(4×2) (+54)(2×1)(8×3)(6×2)(8×2)	or
Cs	(+55)(2×1)(8×3)(6×2)(8×2)(1)	
Ba	(+56)(2×1)(8×3)(6×2)(8×2)(2)	
La	(+57)(2×1)(8×3)(6×2)(8×2)(3)	
Ce	(+58)(2×1)(8×3)(6×2)(8×2)(4) (+58)(2×1)(8×3)(1×3+5×2)(8×2)(3)	and
Pr	(+59)(2×1)(8×3)(1×3+5×2)(8×2)(4) (+59)(2×1)(8×3)(2×3+4×2)(8×2)(3)	In Pro ₂ and
Nd	(+60)(2×1)(8×3)(3×3+3×2)(8×2)(3)	
—	(+61)(2×1)(8×3)(4×3+2×2)(8×2)(3)	
Sa	(+62)(2×1)(8×3)(5×3+1×2)(8×2)(3)	
Eu	(+63)(2×1)(8×3)(6×3)(8×2)(3)	
Gd	(+64)(2×1)(8×3)(6×3)(1×3+7×2)(3)	
Tb	(+65)(2×1)(8×3)(6×3)(2×3+6×2)(3)	
Dy	(+66)(2×1)(8×3)(6×3)(3×3+5×2)(3)	
Ho	(+67)(2×1)(8×3)(6×3)(4×3+4×2)(3)	
Er	(+68)(2×1)(8×3)(6×3)(5×3+3×2)(3)	
TmI	(+69)(2×1)(8×3)(6×3)(6×3+2×2)(3)	
Yb	(+70)(2×1)(8×3)(6×3)(7×3+1×2)(3)	
Lu	(+71)(2×1)(8×3)(6×3)(8×3)(3)	
TmII	(+72)(2×1)(8×3)(6×3)(8×3)(4)	
Ta	(+73)(2×1)(8×3)(6×3)(8×3)(5)	
W	(+74)(2×1)(8×3)(6×3)(8×3)(6) (+74)(2×1)(66+x)(6-x)	and structure uncertain. x=1, 2(?) or 4(?)
—	(+75)(2×1)(8×3)(6×3)(8×3)(7)	and
Os	(+75)(2×1)(66+x)(7-x) (+76)(2×1)(8×3)(6×3)(8×3)(8)	Structure uncertain and

TABLE I continued
Atomic Structures of the Elements

	$(+76)(2 \times 1)(66+x)(8-x)$	Structure uncertain. $x=2$ (?), 4(?), 5(?), or 6(?)
Ir	$(+77)(2 \times 1)(66+x)(9-x)$	Structure uncertain. $x=5$, 6 or 7
Pt	$(+78)(2 \times 1)(66+x)(10-x)$	Structure uncertain. $x=6$ or 8
Au	$(+79)(2 \times 1)(66+x)(11-x)$	Structure uncertain. $x=8$
and	$(+79)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 3)(1)$	
Hg	$(+80)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 3)(2)$	and
	$(+80)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 2)$	or
	$(+80)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 2)(4 \times 2)$	
Tl	$(+81)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 3)(3)$	and
	$(+81)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 2)(1)$	or
	$(+81)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 2)(4 \times 2)(1)$	
Pb	$(+82)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 3)(4)$	and
	$(+82)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 2)(2)$	or
	$(+82)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 2)(4 \times 2)(2)$	
Bi	$(+83)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 3)(5)$	and
	$(+83)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 2)(3) ?$	or
	$(+83)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 2)(4 \times 2)(3) ?$	
Po	$(+84)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 3)(6)$	and
	$(+84)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 2)(4) ?$	or
	$(+84)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 2)(4 \times 2)(4) ?$	
—	$(+85)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 3)(7)$	and
	$(+85)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 2)(5) ?$	or
	$(+85)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 2)(6 \times 2)(4 \times 2)(5) ?$	
Nt	$(+86)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 3)$	
—	$(+87)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 3)(1)$	
Ra	$(+88)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 3)(2)$	
Act	$(+89)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 3)(3)$	
Th	$(+90)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 3)(4)$	
—	$(+91)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 3)(5)$	
U	$(+92)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 3)(6)$	and
	$(+92)(2 \times 1)(8 \times 3)(6 \times 3)(8 \times 3)(6 \times 2)(4 \times 2)(4)$	

to the kernel, making triplets out of pairs, in the manner described above. In different compounds the same element may have different numbers of electrons falling in to the inner shell, the number and arrangement of the valence electrons and of surrounding kernels exerting a great deal of influence. Surrounding the atom in question by oxygen, as in the chromates and permanganates, for instance, tends to keep electrons from dropping in. On the other hand, the max-

TABLE II

Formulae representing Certain Compounds

BF_4^-	(+5) (2×1) (4×2) (4F) -
$\text{Fe}(\text{CN})_6^{----}$	(+26) (2×1) (6×3 + 2×2) (6×2) (6CN) ----
$\text{Fe}(\text{CN})_6^{---}$	(+26) (2×1) (5×3 + 3×2) (6×2) (6CN) ---
$\text{Co}(\text{NH}_3)_6^{+++}$	(+27) (2×1) (6×3 + 2×2) (6×2) (6NH ₃) +++
$\text{Co}(\text{NO}_2)_6^{---}$	(+27) (2×1) (6×3 + 2×2) (6×2) (6NO ₂) ---
Ni^{++}	(+28) (2×1) (4×3 + 2×2) (4×2) ++
$\text{Ni}(\text{CN})_4^{--}$	(+28) (2×1) (4×3 + 2×2) (8×2) (4CN) --
$\text{Ni}(\text{CO})_4$	(+28) (2×1) (6×3) (8×2) (4CO)
$\text{Cu}(\text{NH}_3)_4^{++}$	(+29) (2×1) (5×3 + 1×2) (8×2) (4NH ₃) ++
$\text{Cu}(\text{NH}_3)_2^+$	(+29) (2×1) (6×3) (6×2) (2NH ₃) +
$\text{Zn}(\text{NH}_4)_4^{++}$	(+30) (2×1) (6×3) (8×2) (4NH ₃) ++
$\text{Ag}(\text{NH}_3)_2^{++}$	(+47) (2×1) (8×3) (6×2) (6×2) (2NH ₃) +
ICl_3	(+53) (2×1) (6×3) (8×2) (6×2) (4×2) (3Cl)
I_3^-	$\left[\begin{array}{l} (+53) (2\times 1) (8\times 2) (6\times 2) (8\times 2) \\ (+53) (2\times 1) (6\times 3) (8\times 2) (6\times 2) (4\times 2) \\ (+53) (2\times 1) (8\times 3) (6\times 2) (8\times 2) \end{array} \right]^-$
PtCl_2	(+78) (2×1) (8×3) (6×3) (4×3 + 4×2) (6×2) (2×2) (2Cl)
AuCl_3	(+79) (2×1) (8×3) (6×3) (4×3 + 4×2) (6×2) (3×2) (3Cl)
HAuCl_4	(+79) (2×1) (8×3) (6×3) (4×3 + 4×2) (6×2) (4×2) (3Cl; 4H)
$\text{Au}(\text{CN})_4^-$	(+79) (2×1) (8×3) (6×3) (4×3 + 4×2) (6×2) (4×2) (4CN) -
Hg_2^{++}	[(+80) (2×1) (8×3) (6×3) (8×2) (6×3)] ₂ ++

imum number of electrons which can drop in seems to be reached in the simple positive ions, where there are no other atoms bonded to the atom in question. The number of electrons "drawn in" per atom for each of these elements in its various valences is tabulated in Table IIIA. Note the regularity with which the number drawn in the most stable positive ions increases with an increase in the nuclear charge.

It seems probable that for the first elements, from titanium on, the basic structure is the cube (8×2 or 3), somewhat distorted of course, while at the end of the list the most stable arrangement is the octahedron (6×2 or 3), four of the faces of which are occupied by pairs, which are then arranged at the corners of a tetrahedron (4×2). Crystal structure evidence indicates that iron, cobalt and nickel kernels in some

TABLE III
Electrons drawn in from Valence Shell to Kernel

A.

Ti	0	1	2?	-	-	-	-	-	-	-	-	-
V	0	1	2	3	-	-	-	-	-	-	-	-
Cr	0	-	-	3	4	-	-	-	-	-	-	-
Mn	0	1	-	3	4	5	-	-	-	-	-	-
Fe	-	-	2	-	4 ¹⁾	5	6	-	-	-	-	-
Co	-	-	-	-	-	5 ¹⁾	6	7	-	-	-	-
Ni	-	-	-	-	-	-	6 ¹⁾	7	8	-	-	-
Cu	-	-	-	-	-	-	-	-	-	9	10	-
Zn	-	-	-	-	-	-	-	-	-	-	10	-
Ga	-	-	-	-	-	-	-	-	-	-	10	11
Ge	-	-	-	-	-	-	-	-	-	-	10	12

B.

Zr	0	-	2?	-	-	-	-	-	-	-	-	-
Cb	0	-	2?	-	-	-	-	-	-	-	-	-
Mo	0	1	2	3	-	-	-	-	-	-	-	-
Ru	0	1	2	-	4	5	6	-	-	-	-	-
Rh	-	-	-	-	-	-	6	-	-	-	-	-
Pd	-	-	-	-	-	-	6	-	8	9?	-	-

C.

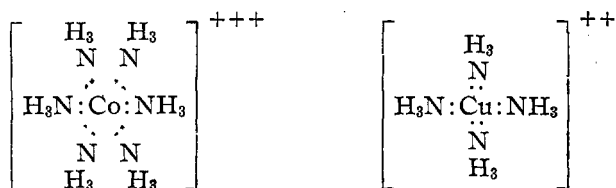
W	0	1	2?	-	4	-	-	-	-	-	-	-
Os	0	-	2?	-	4?	5?	6?	-	-	-	-	-
Ir	0	-	-	-	-	5	6	7	-	-	-	-
Pt	-	-	-	-	-	-	6	-	8	-	-	-
Au	-	-	-	-	-	-	-	-	8	-	10	-

compounds are surrounded by six valence electron-pairs at octahedron corners, indicating a cubical arrangement underlying, and in other compounds by four pairs, probably the result of an octahedron-tetrahedron kernel structure. In most nickel compounds, and in practically all those of copper and the following elements, there are four or a smaller number of pairs in each valence shell. This we may take as indicating a kernel containing a tetrahedron outside of an octahedron. Thus we arrive at the atomic formulae given in Table I.

¹ Evidence from crystal structures indicates that in certain minerals iron, cobalt, and nickel atoms have four electrons each in the valence shell, besides those furnished by other atoms.

The "auxiliary valence" of these elements is merely their tendency or ability to add on compounds with "lone pairs" of electrons (valence pairs not acting as bonds or parts of bonds)

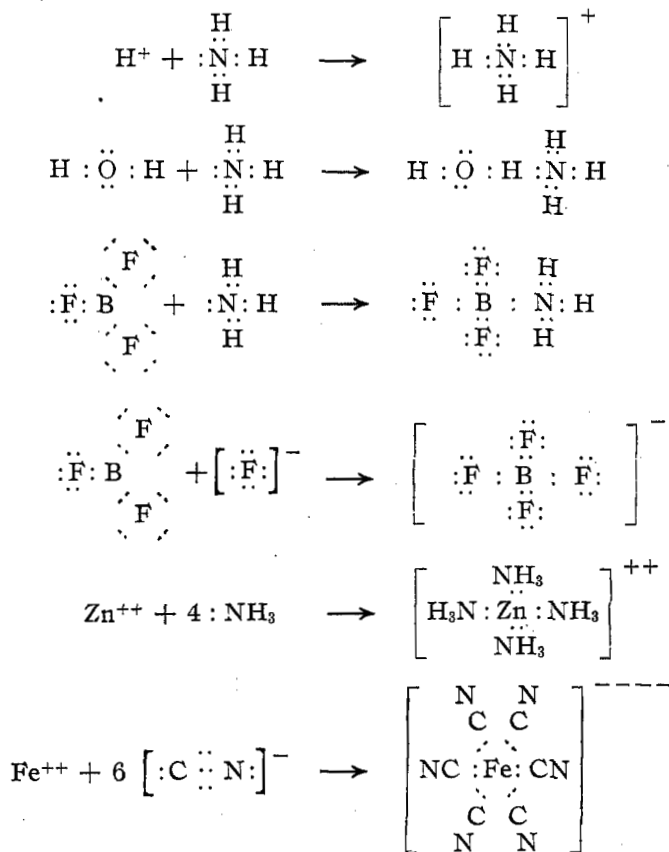
such as trivalent nitrogen compounds $\begin{array}{c} \text{R} \\ \vdots \\ \text{N} \\ \vdots \\ \text{R} \end{array}$, cyanide ion $\begin{array}{c} \text{R} \\ \vdots \\ \text{C} \\ \vdots \\ \text{N} \\ \vdots \\ \text{R} \end{array}$, water $\begin{array}{c} \text{O} \\ \vdots \\ \text{H} \end{array}$, halide ion $\begin{array}{c} \text{X} \\ \vdots \\ \text{X} \end{array}$, etc. These lone pairs occupy positions opposite the centers of the faces of the underlying structure (cube or octahedron), forming, in the case of the iron and cobalt complexes, a valence octahedron, and in the case of the copper, zinc, and some of the nickel complexes, a (distorted) cube consisting of four valence pairs and four kernel pairs, outside of the underlying octahedron. To illustrate this a few of the "kernel formulae" of these compounds are given in Table II. Where it is only desired to indicate the valence electrons, formulae like the following will also sometimes be found useful:



Single bonds, it may be noted here, may be formed in either of three different ways: (1) by the union of two atoms each of which contains a lone (unpaired) electron, (2) by the union of an atom containing a lone pair with another atom capable of holding onto that pair, and (3) by the breaking up of a polyatomic polyelectronic bond, which bond is often formed as the result of the addition of two simple diatomic bonds, but, being usually quite unstable, exists only momentarily as an intermediate step in the reaction.¹

¹ It is important that the reader bear in mind throughout this discussion that a tetrahedron has four corners and four faces, a cube has eight corners and 6 faces, and an octahedron has 6 corners and eight faces.

We are concerned at this point in the development of the present theory, only with reactions of the second type given above. Of these, the following are typical examples:



As one modification of the above reaction we have the reaction of a positively charged kernel containing no electrons in its valence shell with an atom containing a lone valence pair. The bond formed is here often very weak, since the attraction of the positive kernel for electrons is usually small.

This type of reaction is of major importance in crystal formation. In this process each atom or molecule is acted on by several forces tending to form bonds in this way. Indi-

vidually these forces may be quite weak, but collectively they are quite sufficient to pull the atom or molecule into its proper position in the crystal. Once formed, these new bonds may be just as strong as, and even identically the same as, some of the bonds which originally (in the liquid or gaseous state) held the atoms of the molecule together.

It is also this kind of reaction which often produces polymerization and the formation of molecular aggregates (e. g., of H_2O).

The "simple" or first order compounds of elements (Cu, Zn, etc.) which are capable of adding lone pairs in this way have, as a general rule, high melting points, and often are very insoluble, both in water and other solvents, indicating that their crystal structures are very stable and hard to disrupt.

From cuprous copper to krypton, valence electrons occupy positions opposite the four faces of the inner octahedron which are not already occupied by pairs. They thus tend to form another tetrahedron, which is complete in bromide ion and krypton. This and the tetrahedron already there form a cube.

The elements copper, zinc and gallium, although mono-di-, and trivalent, respectively, show a much greater tendency to add electrons and a much smaller tendency to give up their own (forming simple positive ions) than do potassium, calcium and scandium. The reason is that in atoms of the former elements the valence electrons can assume positions around the kernel octahedron which are but slightly farther from the nucleus than the electron-pairs in the kernel tetrahedron; this tetrahedron may then almost be considered as a part of the valence shell; and the *effective* kernel charge—a rough measure of the restoring force acting on a valence electron-pair pulled out slightly from its equilibrium position in a radial direction—is then much greater than in atoms of the alkali or alkaline earth metals.

There seems to be a very slight tendency in di- (and mono-?) valent gallium, and perhaps in divalent germanium, for two

more electrons to be drawn into the kernel, forming, presumably, two more triplets.

Rubidium to Xenon

The elements immediately following krypton, (+ 36) $(2 \times 1) (6 \times 3) (8 \times 2)$, are in every way similar to those following argon, a new shell being gradually built up on the outside of the krypton kernel. It is possible, although not necessary to the theory, that, under the influence of external forces, the cube and the octahedron may in some compounds (e. g., MoO_4^- and RuO_4) exchange places, each corner of the cube passing, in the shift, through a face of the octahedron, and each corner of the octahedron through a face of the cube.

As with the elements following scandium, as soon as the nuclear charge becomes great enough, electrons are pulled in from the valence shell to change pairs to triplets in the next inner shell. This process may begin with zirconium, in its dihydride, and columbium, in its trivalent compounds; most certainly it takes place in molybdenum compounds, the number of electrons drawn in varying from zero in MoO_4^{--} and MoF_6 , to three, in MoCl_3 , etc.

Table IIIB gives the number of electrons which are apparently drawn in per atom for the elements from Zr to Pd. It will be noticed that there is somewhat less regularity here than in the former case (Table IIIA). This and the fact that somewhere in the process the most stable arrangement becomes one of three shells (besides the innermost two electrons)—cube, octahedron and tetrahedron—makes an attempt to give an exact kernel structure for each of these elements in each valence little more than a guess. Hence kernel formulae are not given for these substances in Table I.

By the time silver is reached, however, the rearrangement has been completed and valence electrons begin to form a new shell on the outside of a kernel which we may represent as (+ N) $(2 \times 1) (8 \times 3) (6 \times 2) (4 \times 2)$. These valence electrons take up positions opposite the unoccupied faces of the octahedron, (6×2) , completing the cube around it in

iodide ion and xenon. This is exactly what we found took place in the elements copper to krypton; and the properties of the two groups of elements are strikingly parallel.

Beginning with indium, another kernel arrangement is stable, the formula for which is $(+N) (2 \times 1) (6 \times 3) (8 \times 2) (6 \times 2)$, or, possibly, $(+N) (2 \times 1) (4 \times 3 + 4 \times 2) (6 \times 3) (4 \times 2)$. The kernels of monovalent indium and divalent tin are probably of this type. Iodine, in such substances as I^- and ICl_3 seems to exist in a form in which there are only five electrons in the valence shell, hence we may give it also this kernel formula; and we *may* also be justified in doing the same for trivalent antimony and tetravalent tellurium.

Cesium to Uranium

Xenon, cesium, barium, lanthanum and tetravalent cerium all have kernel structures $(+N) (2 \times 1) (8 \times 3) (6 \times 2) (8 \times 2)$. The properties of these elements correspond closely to those of the elements krypton to zirconium. At cerium the nuclear charge is again great enough to draw in electrons from the valence shell. Cerium is both tri- and tetravalent, and the next thirteen elements (the rest of the rare earths) are invariably trivalent, with the probable exception of praseodymium in the compound PrO_2 , indicating that the increase on the charge on the nucleus from one element to the next is just sufficient to cause one more electron to fall in and make another triplet. This regularity may be attributed to the fact that no intra-kernel rearrangement occurs other than the formation of triplets from pairs, and that the kernel has not a great attraction for electrons and hence is but slightly affected by atoms and electrons outside of it, which was not so true in the other cases where the electrons were drawn in.

When fourteen electrons have fallen into the kernel, all of the pairs have become triplets; further increase in nuclear charge must therefore result in an increase in the number of valence electrons. Thulium II should have a valence of four; tantalum, we know, is pentavalent like columbium; tungsten

is in many of its compounds hexavalent; and osmium is octavalent in the tetroxide.

But here we find that electrons are once more drawn in to the kernel, this time irregularly (Table IIIC), indicating, as before, some sort of a rearrangement of shells. Again the present theory does not enable us to give to each element in each of its valences a definite structure which we can reasonably be sure is correct, until we come to gold.

In its trivalent form the gold kernel is like that of divalent platinum (see Table II). In its monovalent compounds it has, no doubt, either of the two following structures:

(+ 79) $(2 \times 1) (8 \times 3) (6 \times 3) (8 \times 2) (6 \times 3) (1)$ or (+ 79) $(2 \times 1) (6 \times 3) (8 \times 3) (6 \times 3) (8 \times 2) (1)$.

If, as seems likely, the continuity of the curves obtained when the square roots of the frequencies of the L series of X-radiations are plotted against atomic numbers, means that the second shell out from the nucleus remains essentially the same for all elements from zinc to uranium, then the second of these structures is eliminated.¹ Hence we shall provisionally assume the former arrangement.

The addition of two more electrons to the kernel makes the structure (+ N) $(2 \times 1) (8 \times 3) (6 \times 3) (8 \times 3) (6 \times 2)$ (or perhaps, (+ N) $(2 \times 1) (8 \times 3) (6 \times 3) (8 \times 2) (6 \times 2) (4 \times 2)$) possible. Mercury, in the liquid and gaseous states, has no doubt this structure. Were it not for the possibility of shifting to the other form (+ N) $(2 \times 1) (8 \times 3) (6 \times 3) (8 \times 2) (6 \times 3) (2)$, we might find mercury a member of the inert gas group of elements. In all of its compounds the mercury atom possesses two valence electrons, two metal atoms being bonded together in all mercurous compounds, as shown for mercurous ion (Hg_2)⁺⁺, in Table II.

Thallium, lead, and bismuth each form two series of compounds, corresponding to the two possible kernel arrange-

¹ If this assumption is correct, monovalent indium, divalent tin, etc., should each show a different L series spectrum from that obtained from these elements in compounds in which they exhibit their higher valences. To the author's knowledge, this has not been tested experimentally.

ments. In its monovalent compounds thallium has the properties of an alkali metal, which is striking evidence of the fact that its kernel is structurally very similar to those of the rare gases.

Niton, atomic number 86, has the structure (+ N) $(2 \times 1) (8 \times 3) (6 \times 3) (8 \times 3) (6 \times 3)$; and since there is no other stable arrangement to which it can shift (as there is in the case of mercury), it is one of the inert gases, having no tendency either to give up or to add on electrons.

Radium, thorium and uranium, in their compounds, show that they have two, four, and six valence electrons, respectively, indicating that they each have a kernel like that of niton. Uranium in its tetravalent compounds may have either a lone valence pair, or, as seems more likely, the structure $(+ 92) (2 \times 1) (8 \times 3) (6 \times 3) (8 \times 3) (6 \times 2) (4 \times 2) (4)$.

Laws of Force

We shall now return to the consideration of the laws of force between electrons and between nuclei and electrons. Although no attempt will be made in this paper to ascertain just what the true laws of force are at small distances, still it should be of interest to show, by a simple example, how the formation of pairs and triplets is the direct result of the type of law assumed.

In Fig. 1 are shown some curves representing laws of force. Each of these, except *h*, possesses a maximum followed by a decrease in the force as the distance decreases from that corresponding to the maximum. Curves *a* to *g*, inclusive, represent the following equations, in order:

$$f = \frac{ee'}{r^2} \epsilon^{-\frac{2}{r}}, f = \frac{ee'}{r^2} \epsilon^{-\frac{1}{r^2}}, f = \frac{ee'}{r^2} \epsilon^{-\frac{2}{r} + \frac{0.1}{r^2}}, f = \frac{ee'r}{r^3 + 1},$$

$$f = \frac{ee'r^2}{r^4 + 1}, f = \frac{ee'(r^2 + 0.02)}{r^4 + 1}, f = ee' \left(\frac{1}{r^2} - \frac{0.667}{r^3} \right).$$

In each of the above, *r* is the distance between the two charges *e* and *e'* the magnitude of the charges, ϵ is the base of natural logarithms. In plotting the curves, *e* and *e'* were taken as unity. Curves *a* and *h* are of types suggested by Lewis;¹ *g* is

¹ G. N. Lewis: *Science*, **46**, 297 (1917).

of a type used by J. J. Thomson¹ Langmuir² and others; j represents Coulomb's law.

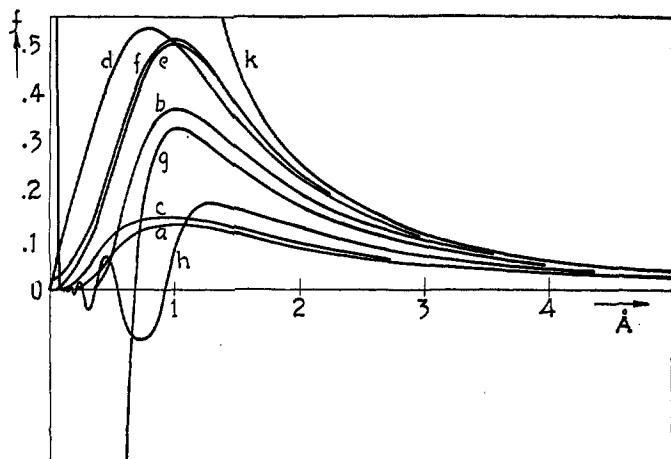


Fig. 1

Let us now assume that both repulsion between two electrons and attraction between a nucleus and an electron obey the law represented by curve e .

Lithium

From the equation

$$\frac{3r^2}{r^4 + 1} = \frac{2 \times 0.866 \times 1.732^2 r^2}{1.732^4 r^4 + 1}$$

we can obtain $r = 0.564 \text{ \AA.}$ as the equilibrium distance of each of three symmetrically placed electrons from the nucleus. By a rather laborious combined graphical and analytical method it may be shown that if one electron is displaced *slightly* toward one of the others, the resultant force acting on it will tend to return it to its previous symmetrical position; but if two electrons approach each other closer than about 0.37 \AA. , the resultant force tends to force them still closer together, until, as a matter of fact, they are coincident.

¹ Phil. Mag., **41**, 510 (1921).

² Science, **53**, 290 (1921).

If we assume a slightly different law, say $f = \frac{ee'(r^2 + 0.02)}{r^4 + 1}$

(Curve *f*, Fig. 1), coincidence will not result. There will then be two equilibrium arrangements, one with the three electrons at the corners of an equilateral triangle, each



Fig. 2

at a distance of 0.548 Å., the other with two electrons 0.39 Å. from the nucleus and 0.10 Å. from each other and the third electron at a distance of 0.61 Å. from the nucleus. (Fig. 2.)

Beryllium and Boron

It may similarly be shown that in an atom of beryllium or boron, were the same law of force acting, there would be two equilibrium configurations, one the symmetrical arrangement, the other an arrangement in which two of the electrons are paired. The distances between the charges in these assumed structures may be computed, but for our present purpose they are unimportant.

It is easy to see how the actual law of force might make only the unsymmetrical disposition stable, or how even with the assumed law, oscillations of the electrons might have the same result.

Carbon and Nitrogen

If we assume that the inner pair of electrons in carbon acts in every way as though a part of the nucleus, the computation for carbon is just like that for beryllium and there are again two stable arrangements for the four outer electrons. For some reason, however, the unsymmetrical configuration is rarely, if ever, assumed. This may be because of the two inner electrons tending to prevent the shift, or merely because we have not made the right assumptions with regard to the law of force.

In nitrogen, because of the fact that the nuclear charge is greater and because in the most symmetrical disposition five electrons must be much closer to each other than four, pairing of two of the valence electrons must occur.

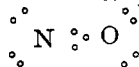
Other Elements; Triplets; Four-electron Groups

Pairing in other elements occurs in the same way, and for similar reasons as in the elements just considered. In a corresponding manner also, if two pairs in the same or different atomic shells are forced close enough together, one of the electrons in one pair will join the two in the other pair, forming a triplet. This leaves a single electron, which immediately pairs off with another (usually one from the valence shell). Also, if a single electron in the valence shell is drawn within the distance of maximum repulsion from a pair in the outermost kernel shell, the single valence electron will drop into the kernel, forming a triplet.

In case two triplets, or a pair and a triplet, were pulled sufficiently close to each other, we should expect from similar reasoning that a group of four electrons would be formed; but the author has been unable to work out a concordant system of structures on such a basis, hence we may assume that even in the heaviest elements the nuclear pull on electrons is not strong enough to accomplish such a result.

The Three-electron Bond

There is nothing contrary to this theory in the idea of a three-electron bond. Such a bond between two atoms, however, could only be stable if the three electrons joined two kernels which both had a strong attraction for electrons but which did not repel each other with too great a force. Such a condition is met with in the compound NO. Although both kernels maintain a strong hold on the bond between them, their mutual repulsion causes them to be forced closer to the remaining electrons. Because of the strong attraction of each kernel for these they are drawn in so close that if they were arranged at the points of tetrahedra, as in most nitrogen and oxygen compounds they would be somewhat closer to each other than the distance of maximum repulsion. Hence triangles of electron-groups are formed around both kernels. The compounds might be represented in this way:



Similarly we might give

NO_2 the structure $\begin{array}{c} \text{O} \text{---} \text{N} \text{---} \text{O} \\ \text{..} \quad \text{..} \quad \text{..} \end{array}$. The addition of the second

oxygen atom to the compound increases the distance between the points of the triangle around the nitrogen, and also around the oxygen. The whole structure is less stable and more reactive; the electrons of the lone pairs are less firmly held in position at the corners of the triangles. Hence the substance is colored and tends to polymerize to N_2O_4 .

There seems to be little or no evidence of three electrons acting as a single bond between any other two elements, but evidence is presented elsewhere by the author¹ of bonds joining more than two atoms which consist of three, four, five, six, seven, or even eight electrons.

The Stability of the Pair

The fact that a large majority of known compounds contain (outside of the atomic nuclei) a total number of electrons which is even, and that among those compounds which contain only elements of comparatively small atomic weight, an "odd molecule" is almost invariably colored, reactive and unstable, has led many to believe that there is something inherently stable about the *pair* of electrons both in chemical bonds and in atomic kernels. But the theory developed in this paper shows that this is not necessarily the case. Under certain conditions—in the inner shells of atoms with large nuclear charges—the triplet is stable and the pair is unstable. In all of the lighter atoms and in the valence shells of all atoms, it is true, the pair tends to form rather than triplet. Away from the influence of positive charges, electrons show no tendency even to pair.

Since triplets exist mainly, if not entirely, in the kernels of the heavier atoms, and since the stable shells of triplets are those containing an even number (6 or 8) of groups, in compounds of these elements also the total number of electrons is

¹ Huggins: Jour. Am. Chem. Soc., August, 1922; Science, July, 1922.

even, *except* where the process which has been styled the "dropping in" of electrons is taking place—where shells of pairs are but partly changed to shells of triplets. Whenever an *odd* number of electrons has "fallen in" to the kernel—that is, when the kernel contains an *odd* number of triplets—the total number of electrons in the compounds of that element in that particular valence will be odd, unless, of course, there are two such elements in the compound. In these cases the odd number of electrons is not accompanied by instability, reactivity, and intense color, unless these are due to other causes.

This theory, then, not only explains the cause of an even total number of electrons in so many compounds, but specifies in what compounds there will be an odd number, and whether or not the odd molecule will be unstable, highly colored and very reactive.

Electronic Positions; Spectroscopy

The "positions" of electrons in the various atoms which have been presented in this paper should of course be considered merely as equilibrium positions, about which there may be oscillation or rotation of the electrons or electron groups.

Since the actual laws of force acting between the elementary positive and negative charges are still unknown to us, we cannot at the present time compute the distances between electrons in the pairs and triplets and the radii of the various shells in the atoms of each element. For the same reason this theory in its present form cannot be checked up by means of spectroscopic facts. It is to be hoped, however, that the limitations which the theory seems to place on the variations of the force laws at small distances, will aid in the search for the truth regarding them.

Summary

The Lewis theory of valence and atomic structure is assumed to be correct for the lighter atoms. The evidence in favor of a tetrahedron of electron-pairs, rather than a cube of single electrons, being the most stable arrangement for the valence shell in these atoms—an idea also proposed by Lewis—

is presented. It is shown how the stability of such an arrangement may be the result of the deviation of the force law between two electrons from Coulomb's law at small distances. The chief requirement for this purpose is "that as two electrons approach each other, the repulsion between them reaches a maximum at a distance of the order of magnitude of 1 \AA , the force then decreasing, for a considerable proportion of the remaining distance, at least." As result of a law of this type, whenever two electrons, forming part of an atomic shell, are forced close enough together, they come still closer to each other—that is, they pair off—and when two pairs, or a pair by the attraction of an atomic nucleus and the repulsion of other electrons, a triplet is formed. Based on this assumption and on the idea that the electrons in an atomic shell tend to place themselves opposite the centers of the faces of the imaginary polyhedron formed by the electron groups in the next underlying kernel shell, an arrangement of electrons is obtained for each element in each of its valences (with a very few exceptions, not yet completely worked out) which conforms to the known properties of that element. For these arrangements Table I may be consulted. Periodic relationships are also simply and logically accounted for.

The author wishes to here express his grateful appreciation of the kindly criticism and advice received from other members of this Department, especially Professors G. N. Lewis and Wm. C. Bray.

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