LANGMUIR'S THEORY OF THE ARRANGEMENT OF ELECTRONS IN ATOMS AND MOLECULES.

By CHARLES R. BURY.

Langmuir[1] pictures an atom as consisting of a positively charged nucleus and electrons, equal in number to the units of positive electricity with which the nucleus is charged (or the atomic number of the element), which are arranged in concentric spherical shells of equal thickness round the nucleus. The electrons, though free to rotate or oscillate about their mean positions, are definitely localized in the atom. They are situated in cells, all of equal volume in any given atom: since there are 2 cells in the inner shell, there will be 8 in the second, 18 in the third and 32 in the fourth.

In his fourth postulate, Langmuir states that each cell can contain two electrons, except the two cells in the inner shell, which can contain only one: and that there can be no electrons in the outer shell until all the inner shells contain their maximum numbers of electrons.

By substituting an alternative to this fourth postulate it is possible to get a series of atomic structures similar to those obtained by Langmuir for the elements of lower atomic weight than sodium, but different for those of higher atomic weight. These structures are preferred by the author for the following reasons: (1) they give a better explanation of the chemical properties of the elements; (2) the necessity of postulating cells "independent of the electrons in them" is avoided. At the same time, the inconsistency that some cells can contain two electrons, others only one, is also avoided. The alternative postulate is as follows. The maximum number of electrons in each shell or layer is proportional to the area of its surface; thus, successive layers can contain 2, 8, 18 and 32 electrons. Groups of 8 and 18 electrons in a layer are stable, even when that layer can contain a larger number of electrons. The maximum number of electrons in the outer layer of an atom is 8: more than 8 electrons can exist in a shell only when there is an accumulation of electrons in an outer layer. During the change of an inner layer from a stable group of 8 to one of 18, or from 18 to 32, there occurs a transition series of elements which can have more than one structure.

The Two Short Periods.—This postulate will leave unaltered the structures assigned by Langmuir to the elements of the first short period.

Sodium will have 2 electrons in the inner layer, 8 in the second, and one in the third; an arrangement that can conveniently be abbreviated as

[1] Langmuir, THIS JOURNAL, 41, 868 (1919).

(2,8,1). The succeeding elements in the second short period will each have one more electron in the third layer, up to argon with the structure (2,8,8), its chemical properties being attributed to the stability of the group of 8, not to the outer layer being complete, for the third layer can contain 18 electrons. For the structure of the elements of this period, Langmuir doubles the electrons in the cells of the second layer. The proposed alteration of structure suggests no difference in chemical properties from those deduced by Langmuir.

The First Long period.—Since 8 is the maximum number of electrons in the outer layer, potassium, calcium and scandium must form a fourth layer, although their third is not complete. Their structures will be (2,8,8,1), (2,8,8,2) and (2,8,8,3).

The elements from titanium to copper form a transition series, in which the stable but incomplete group of 8 in the third layer is changed to a saturated group of 18. With the accumulation of 4 electrons in the fourth layer of titanium, there is the possibility of some of them passing into the third unsaturated layer. These transition elements can have more than one structure, and the following are possible structures that the elements assume in their various compounds.

Ti	(2,8,8,4)	(2,8,9,3)	(2,8,10,2)		
V	(2,8,8,5)	(2,8,9,4)	(2,8,10,3)	(2,8,11,2)	
Cr	(2,8,8,6)	(2,8,11,3)	(2,8,12,2)		
Mn	(2,8,8,7)	(2,8,9,6)	(2,8,11,4)	(2,8,12,3)	(2,8,13,2)
Fe	(2,8,10,6)	(2,8,12,4)	(2,8,13,3)	(2,8,14,2)	
Co	(2,8,13,4)	(2,8,14,3)	(2,8,15,2)		
Ni	(2,8,14,4)	(2,8,15,3)	(2,8,16,2)		
Cu	(2,8,17,2)	(2,8,18,1)			

Of course, many more possibilities might be predicted. The question why only stable compounds corresponding with some of the possibilities exist and why unstable compounds correspond with others, while some possibilities are not represented in any known compounds, can be only partly answered. An accumulation of 4 electrons in the outer layer suffices in favorable circumstances to send one of them into the inner layer, but the tendency for one out of a group of 3 electrons to pass into the inner layer will be much less, while the tendency for 2 electrons to force one of themselves into the inner layer will be very small. This accounts for the great instability of the divalent salts of titanium, vanadium and chromium, in which they will have the structures (2,8,10,2), (2,8,11,2) and (2,8,12,2). Only one element, copper, forms a series of monovalent salts, in which it will have the structure (2,8,18,1), this structure being made possible by the stable group of 18 in the third layer. On the other hand, once several electrons have been forced into the third layer, the group of 8 is destroyed, and further electrons do not meet with the same resistance in passing into the third layer. Finally, in cobalt, nickel

and copper, the stable group of 8 in the third layer is impossible: such a structure would involve more than 8 electrons in the fourth, or the formation of a fifth layer. Electrons meet with little resistance in passing into the inner layer: the elements have no tendency to form compounds in which they exhibit a high valence, and their divalent salts are found to be the most stable.

The octet theory of valence in its plain straightforward form applies to the compounds of these elements: and this method of treatment compares favorably for practical convenience and simplicity with the elaborate arrangement of electrons in molecules which Langmuir's structures demand for the elements, while at the same time it affords a satisfactory explanation of their chemical properties. Thus manganese, in the permanganates, has the structure (2,8,8,7), and differs from chlorine (2,8,7), in its kernel only, just as chlorine differs from bromine, but not in the outer layer of electrons, on which the valence and type of compound depend. In chromates, manganates and ferrates, the metals have the structure (2,8,8,6), (2,8,9,6) and (2,8,10,6), having the same outer larey as sulfur (2,8,6) or selenium (2,8,18,6), but their kernels resemble each other far more than they resemble the kernels of sulfur or selenium; consequently, while they resemble sulfates and selenates, they resemble each other more closely. If Langmuir's structures for these elements are accepted, they should show no more resemblance than such series as carbon dioxide, nitrogen peroxide and ozone, or silica, phosphorus tetroxide, sulfur dioxide and chlorine peroxide. In the manganites, ferrites and in the dioxides of manganese, iron, cobalt, and nickel, the metals have 4 electrons in their outer layers. In their trivalent salts which all the transition elements except copper form, they have three electrons in their outer layers; and in their divalent salts, which they all form, they have only two. Throughout this transition series of elements, similar compounds are attributed to the elements having a similar outer layer of electrons, and differing only in their kernels.

It seems impossible to give a rational explanation of the chemical properties of such an element as manganese unless the possibility of more than one structure is postulated. Langmuir is driven to inconsistency in attempting to ascribe a structure to sodium manganate. Its chemical properties demand that the manganese atom should form an octet, but there is one electron too many. According to Langmuir's postulates there is no room for it in the inner layers; he has to invent a fresh position for electrons in the atom; the extra electron is held prisoner between the kernel and the octet which the manganese atom holds in common with the 4 oxygen atoms. If the structure of manganese is regarded as invariable, divalent salts, such as manganous chloride, present even greater difficulties. Such a compound would be formed by one electron passing

from the outer layer of the manganese atom to each of the two chlorine atoms, leaving 5 free electrons in the outer shell of the manganese atom. No octet is formed round the manganese atom in which these 5 could be held prisoner. Free electrons in the outer shell of an atom cause a substance containing that atom to be highly reactive, yet manganous salts are probably the most stable compounds of manganese.

Lewis[2] in his hypothesis of the cubical atom expresses the opinion that in these elements "the kernel of the atom is not uniquely and permanently defined." In his magneton theory of the structure of the atom, Parson[3] uses the conception of "tautomerism" in the structure of the atom to account for the structure of the elements of the first long period.

The remaining elements of this period have their 3 inner shells complete. Zinc will have the structure (2,8,18,2): there is no possibility of change of structure, and it is therefore a normal element and resembles magnesium and glucinum, the two normal elements of lower atomic weight that have two electrons in the outer layer. Each succeeding element in the period will have one more electron in the fourth shell. Krypton will have the structure (2,8,18,8) and, like argon, owes its chemical properties to the stability of the group of 8 in the outer layer, although this fourth layer is unsaturated, for it can hold 32 electrons.

The Second Long Period.—The chemical properties of this group seem to indicate that the groups of 8 and 18 electrons in the fourth layer are more stable than they were in the third.

Rubidium (2,8,18,8,1), strontium (2,8,18,8,2), and yttrium (2,8,18,8,3) are analogous to potassium, calcium and scandium. A fifth layer is being built over an incomplete fourth shell.

The electrons in the outer layers of zirconium, columbium and molybdenum show little tendency to pass into the inner layers. Their chemical properties, so far as they are known, seem to be explained by one structure only for each element, (2,8,18,8,4), (2,8,18,8,5) and (2,8,18,8,6), respectively. In this they differ from the elements preceding them in their respective groups, titanium, vanadium and chromium. Those compounds in which they exhibit their highest valence are relatively more numerous, and in these alone do they resemble the elements of the first long period. The divalent salts of molybdenum, which are probably complexes of more elaborate constitution than their simple empirical formulas would suggest, are very different from the divalent salts of the transition elements of the first long period. Molybdates have not the same oxidizing properties that the chromates have.

No element of atomic number 43, corresponding to manganese, has as yet been discovered.

[2] Lewis, THIS JOURNAL, **38**, 785 (1916).

[3] Parson, *Smithsonian Misc. Coll.*, **65**, No. 11, p. 23 (1915).

The fact that ruthenium forms a tetroxide, in which it must have the structure (2,8,18,8,8), shows that in this period the electrons pass into the inner layer less readily than in the first long period, for iron shows no sign of having a similar structure.

Again, possibly owing to the greater stability of the group of 18 electrons in the fourth shell, silver forms only monovalent salts, in which it must have the structure (2,8,18,18,1); unlike copper, it shows no tendency to form divalent salts in which it would have the structure (2,8,18,17,2). This causes the process of transition from a group of 8 to one of 18 electrons in the fourth shell to be much shorter, and to be more sudden than it was in the third shell. In the first long period, there were 8 transition elements; in the second long period there are only 3, ruthenium, rhodium and palladium; and these show but little resemblance to their analogs in the first long period, iron, cobalt and nickel. As transition elements, they may have different structures in their different compounds, and the following possibilities can be recognized:

Ru (2,8,18,8,8) (2,8,18,9,7) (2,8,18,10,6) (2,8,18,12,4) (2,8,18,13,3) (2,8,18,14,2)
Rh (2,8,18,11,6) (2,8,18,13,4) (2,8,18,14,3) (2,8,18,15,2)
Pd (2,8,18,14,4) (2,8,18,15,3) (2,8,18,16,2)

As in the previous transition series in the first long period, the lower valences of the first transition elements lead to the formation of unstable compounds; ruthenium and rhodium divalent salts are unstable. The last transition element, palladium, shows the same preference for the lower valences that is characteristic of cobalt and nickel; palladium trioxide and its derivatives are unknown, and palladium alone, of this series, forms stable divalent salts. In this transition series, it is a rule, not without exceptions, that those structures that contain an even number of electrons in the fourth shell lead to the formation of the most stable compounds.

Silver has the structure (2,8,18,18,1): the fourth shell is still incomplete, for it can contain 32 electrons. It nevertheless contains a stable group of 18. This stable but incomplete group of 18 electrons in the fourth shell remains to the end of the second long period, each succeeding element having one more electron in the fifth layer. It is possible that such compounds as cadmous oxide (Cd_2O), indium dichloride, and the stannous salts might be ascribed to electrons passing from the fifth to the incomplete fourth layer, but no such possibility can account for the existence of gallium and germanium dichlorides. The last elements of this period form compounds by completing the octet in the fifth layer; and the transition from 18 to 32 electrons in the fourth shell does not occur till the next period.

Xenon will have the structure (2,8,18,18,8).

The Rare Earth Period.—Cesium, barium and lanthanum will have the structures (2,8,18,18,8,1), (2,8,18,18,8,2) and (2,8,18,18,8,3) respectively, a sixth layer being built over incomplete but stable groups of 18 and 8 electrons in the fourth and fifth shells.

Number of electrons in outer shell of atoms																									Number of electrons in successive shells of kernel
0	1	2	3	4	5	6	variable		3	4	5	6	7	variable	1	2	3	4	5	6	7	8		
H																						He	0.	
He	Li																					Ne	2.	
Ne	Na														Be	B	C	N	O	F		A	2,8.	
A	K	Ca					Sc								Mg	Al	Si	P	S	Cl			2,8,8.	
							(Ti V Cr Mn Fe Co Ni Cu)																variable; 1st 8-18 transition series	
															Zn	Ga	Ge	As	Se	Br	Kr		2,8,18.	
Xe	Rb	Sr					Y	Zr	Cb	Mo	43												2,8,18,8.	
							(Ru Rh Pd)																variable: 2nd 8-18 transition series	
													Ag	Cd	In	Sn	Sb	Te	I	Xe			2,8,18,18.	
Xe	Cs	Ba	La																				2,8,18,18,8.	
			Ce .... Yb																				variable: 1st 18-32 transition series	
							Lu 72 Ta W 75																2,8,18,32,8.	
							(Os Ir Pt Au)																variable; 3rd 8-18 transition series	
												Hg	Tl	Pb	Bi	Po	85	Nt					2,8,18,32,18	
Nt	87	Ra	Ac	Th	Bv	U																	2,8,18,32,18,8.	

Periodic arrangement of the elements and structure of their atoms. No attempt to represent the variable structures of the four transition series has been made.

Cerium is the first of a transition series in which the group of 18 electrons in the fourth layer is changed to one of 32. In previous transition series, succeeding elements have differed in similar compounds only by one electron in the outer shell of their kernels: in this series they will differ only by one electron in an inner shell, the fourth, of their kernels. The elements will therefore resemble each other in similar compounds even more closely than, for example, manganese, iron, cobalt, nickel and copper in their divalent salts. A second feature of this transition series is that the elements do not show that variety of structure that is found in other transition series, though a few elements show signs of having more than one structure. The following structures are suggested.

Ce	(2,8,18,18,8,4)	(2,8,18,19,8,3)
Pr	(2,8,18,19,8,4)	(2,8,18,20,8,3)
Nd	(2,8,18,21,8,3)	
Undiscovered element of atomic number 61.	(2,8,18,22,8,3)	
Sa	(2,8,18,23,8,3)	(2,8,18,24,8,2)
Eu	(2,8,18,24,8,3)	(2,8,18,25,8,2)
Gd	(2,8,18,25,8,3)	

So far as their chemical properties are known, the remaining seven rare earths show no sign of having more than one structure. Each succeeding element will have one more electron in the fourth shell. Lutecium, the rare earth of highest atomic weight, will have the structure (2,8,18,32,8,3); the fourth shell is now complete, and it will be a normal element. Lutecium, rather than lanthanum (2,8,18,18,8,3), resembles scandium (2,8,8,3) and yttrium (2,8,18,8,3), just as, in the first long period, zinc rather than calcium resembles glucinum and magnesium.

Between lutecium and tantalum an element of atomic number 72 is to be expected. This would have the structure (2,8,18,32,8,4), and would resemble zirconium.

Tantalum and tungsten have the structures (2,8,18,32,8,5) and (2,8,18, 32,8,6), and are analogous to columbium and molybdenum. An element of atomic number 75 remains undiscovered.

Osmium, iridium, platinum and possibly gold form a transition series in which the group of 8 in the fifth layer changes to a group of 18 electrons. This third 8–18 transition resembles the second, rather than the first, such transition; and in fact, osmium, iridium, and platinum, resemble ruthenium, rhodium and palladium more than they resemble iron, cobalt and nickel. The various structures which these elements, as transition elements, can assume are probably as follows.

Os (2,8,18,32,8,8) (2,8,18,32,10,6) (2,8,18,32,12,4) (2,8,18,32,13,3) (2,8,18,32,14,2)
Ir (2,8,18,32,11,6) (2,8,18,32,13,4) (2,8,18,32,14,3) (2,8,18,32,15,2)
Pt (2,8,18,32,12,6) (2,8,18,32,14,4) (2,8,18,32,15,3) (2,8,18,32,16,2)
Au (2,8,18,32,16,3) (2,8,18,32,17,2) (2,8,18,32,18,1)

In this transition series also, the first elements have a tendency to form compounds with the highest valences, and the last elements to form compounds with the lower valences. Those compounds in which the metal has an even number of electrons in its fifth shell are generally more stable than when the number of electrons in the fifth layer is odd.

Mercury will have the structure (2,8,18,32,18,2), the 4 inner shells being complete, the fifth containing an incomplete but stable group of 18 electrons. Each succeeding element in this period will have one more electron in the sixth layer, until we come to niton, with the structure (2,8,18,32,18,8).

The Last Period.—Only 5 elements of this period are known, and the chemical properties of only two of them, thorium and uranium, are known well. In this period a second 18–32 transition series may be expected.

The second 8–18 transition series was shorter and more sudden than the first, possibly because of the greater stability of the groups of 8 and 18 electrons in the fourth, than in the third shells; and the elements of the second transition series showed but little resemblance to those of the first. To judge by analogy, the second 18–32 transition series may be expected to begin later, to end earlier, to be shorter and more abrupt than the first 18–32 transition series. Little resemblance between the chemical properties of the elements of the two series is to be expected. Possibly an element, not yet discovered, of atomic number 94, two more than that of uranium, is the first of a series of 7 transition elements that would be metals, something like the ruthenium group but more electropositive. Possibly uranium itself is the first member of this second 18–32 transition

series. The following structures are suggested for the elements of this period.

Ra	(2,8,18,32,18,8,2)	Th	(2,8,18,32,18,8,4)
Ac	(2,8,18,32,18,8,3)	Ux_2	(2,8,18,32,18,8,5)
	U	(2,8,18,32,18,8,6)	

The structures for the elements arrived at are more in harmony with the atomic diameters, determined by Bragg[4] from the study of crystal structure, than are the structures given by Langmuir.

Element.	Atomic diameter in Å. (Bragg).	Number of shells in kernel. (Langmuir).	(Bury).
Lithium.............	3.00	1	1
Sodium..............	3.55	2	2
Potassium...........	4.15	2	3
Rubidium............	4.50	3	4
Cesium..............	4.75	3	5
		Number of shells in atom.	
Fluorine............	1.35	2	2
Chlorine............	2.10	2	3
Bromine.............	2.38	3	4
Iodine..............	2.80	3	5

On the basis of Langmuir's structures for the elements, the difference in atomic diameter between rubidium and potassium might be expected to be more than that between potassium and sodium, for both the latter contain 2 shells of electrons, while rubidium contains 3. On the basis of the atomic structures suggested in this paper, the difference in atomic diameters between any two successive elements in the same group might be expected to be constant.

During the course of preparation of this paper, structures similar to those suggested by the author for the inert gases have been proposed by Bohr,[5] who bases his arguments on the study of emission spectra.

Summary.

An alternative to Langmuir's fourth postulate, in his paper on the arrangement of electrons in atoms and molecules, has been suggested. This avoids the necessity of postulating cells in the structure of the atom, and leads to different structures for the elements of higher atomic weight than neon. It is claimed that the application of Lewis and Langmuir's octet theory of valence to these structures gives a better explanation of the chemical properties of the higher elements, than can be obtained from Langmuir's structures.

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[4] Bragg, *Phil. Mag.*, [6] **40**, 169 (1920).
[5] Bohr, *Nature*, **107**, 106 (1921).