

The Langmuir Postulates—I*

An Intruduction to Dr. Irving Langmuir's New Theory of the Constitution of Atoms and Molecules
By Ellwood Hendrick

THE address of Dr. Irving Langmuir delivered at the Buffalo meeting of the American Chemical Society on "The Arrangement of Electrons in Atoms and Molecules" made such a deep impression upon those who heard it, and the potentialities of the Langmuir postulates loom so large as applied to research, that we resolved to give our readers a report on the subject as soon as this could be made ready. The first original paper appeared in the June number of the *Journal of the American Chemical Society*. Owing to the intense concentration of the text it is not easy reading, even to the average chemist, and in what follows we shall not attempt to cover the field with thoroughness, or even to touch upon problems that require experience in applying the postulates. Our purpose is to write an introductory chapter, and to begin "further back" for the benefit of those who have not followed diligently the voluminous literature of research on the structure of atoms and molecules. We shall not even attempt to make clear between the Langmuir postulates and the work of other men in research whose conclusions are in part accepted. We are dealing with a new philosophy of chemistry which differs from that of the present text-books in various concepts, but which provides a definite means of determining upon the arrangement of atoms in combination, as well as that of electrons in atoms and molecules.

PRACTICAL VALUE OF THE THEORY.

We shall try to give at least a glimpse of its amazing practicality when applied in the laboratory. It is, in effect, a new angle of attack which calls for new mental processes; and, as with any new tool, these seem difficult at first. When we state, however, that with adequate understanding and experience, it becomes possible to predicate the physical and chemical qualities of a substance, even to its crystalline structure, before it is synthesized; that it opens up a new and workable theory of valence; that it explains the curious manifestations of the elements of the rare earths and other elements in the periodic table, the irregularities of nitrogen, and the magnetic properties of the iron and platinum groups of metals, as but a part of its contributions, we need give no further emphasis to its value as an aid to technology as well as to research. We shall not undertake to make all these facts clear. Our purpose is to lure the reader into a consideration of the subject, so that he may approach Dr. Langmuir's present and future papers with that quality of interest which is warranted by their importance.

For lack of space and with a view of confining ourselves to the simplest features in this article we shall omit discussion of the principle involved in the secondary planes (Postulate I) in connection with the position of electrons in atoms of greater complexity, also the magnetic forces as indicated in Postulate V, and the illumination shed upon the great work of Werner, and refer the reader to the first paper in the June number of the *Journal of the American Chemical Society* for the explanations and a much more comprehensive discussion of the entire subject in a very condensed form.

We are indebted to Dr. Langmuir for a number of extended interviews, and we express our sincere obligations to him for his patience in exposition.

STRUCTURAL RESEMBLANCE OF N₂O AND CO₂

By way of indicating the workings of the theory let us take as an example two gasses that we have not heretofore regarded as having any qualities in common: N₂O, or laughing gas, and CO₂. According to the Langmuir postulates, as we shall try to develop them in part, these gasses display a remarkable resemblance in the structure of their molecules, containing each the same balanced number of positive and negative charges, and the same exterior arrangement of electrons, so that, were they magnified to visibility, and the kernels of the atoms hidden from view, we should be unable to tell them apart by looking at them. At least it is a fair guess that by looking at them, under these conditions, we should be unable to distinguish them, one from the other. Then we conclude that they must have certain physical properties in common. The figures which follow have not been published elsewhere at the present writing; we are indebted for them to Dr. Langmuir, who will

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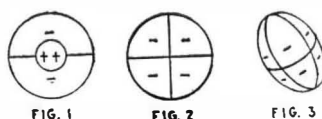
We are laboring under great difficulties on account of the strike of compositors and pressmen. Through no fault of ours the publication of the SCIENTIFIC AMERICAN SUPPLEMENT has been seriously hampered, but despite all handicaps we are endeavoring to continue issuing this journal. Obviously our normal schedules cannot be maintained, and until the strike is ended publication of the SUPPLEMENT will necessarily be much delayed. This week we are offering you a double number, combining the issues of October 4th and 11th. We beg your indulgence in these trying times. We are doing everything in our power to serve your interests.

present them later on with detailed explanation in the *Journal of the American Chemical Society*, but they will serve to indicate the points of remarkable similarity in the physical properties of two gases which Dr. Langmuir concludes to be similar in structure. The records are taken from unrelated pages of published works:

	N ₂ O	CO ₂
Critical pressure, atmospheres	75	77
Critical temperature, deg.C	35.4	31.9
Viscosity at 20 deg.C	148X10 ⁻⁴	148X10 ⁻⁴
Heat conductivity at 100 deg.C	0.0506	0.0506
Density of liquid at -20 deg.C	0.996	1.031
Density of liquid at 10 deg.C	0.856	0.858
Refractive index of liquid, D line 16 deg.C	1.193	1.190
Dielectric constant of liquid at 0 deg.C	1.598	1.582
Magnetic susceptibility of gas at 40 atm., 16 deg.C	0.12X10 ⁻⁶	0.12X10 ⁻⁶
Solubility in water, 0 deg.C	1.305	1.780
Solubility in alcohol, 15 deg.C	3.25	3.13

Both gases form hydrates, N₂O.6H₂O and CO₂.6H₂O. The vapor pressure of the hydrate of N₂O is 5 atmospheres at 6 deg. C., while the hydrate of CO₂ has this vapor pressure at -9 deg.C. The heats of formation of the two hydrates are given respectively as 14,900, and 15,000 calories pergram-molecule.

The surface tension of the liquid N₂O is 2.9 dynes per sq.cm. at 12.2 deg., while CO₂ has this same surface tension at 9.0 deg.C.



Helium

Neon

Thus N₂O at any given temperature has properties practically identical with those of CO₂ at a temperature of 3 deg. lower.

These results indicate the similarity of the outside structure of the molecules.

DISAGREEMENT IN FREEZING POINT.

There is one property, however, that is in marked contrast to those given above: the freezing point of N₂O is -102 deg.C. while that of CO₂ is -56 deg. This may be taken as an indication that the freezing point is a property which is abnormally sensitive to even slight differences in structure. The evidence seems to indicate that CO₂ is slightly more symmetrical and has a slightly weaker external field of force than that of N₂O.

It would be hard to find such an array of coincidences unless there were reasons for them, and it is one of the purposes of this paper to show reasons for them, as we proceed.

All of these figures have been gathered by painstaking research in the past. They were uncorrelated and uninteresting. But in the light of this theory we find them ranging themselves into such subtle correlation as to cause them to function as parts of that greater whole which men of research are ever trying to discover. For decades these figures have been available. But in this case, as in that of other bodies which we shall consider later, the identical physical characteristics of those of like structure have remained unobserved.

II

At the end of the paper we present the postulates upon which the work is based, and we shall refer to

them from time to time as we proceed. But, going "further back," as we promised to do, let us consider every atom as made up of two component parts: the electro-positive charges concentrated in the nucleus of each atom, which is individual and peculiar to each element, and the electrons which are electro-negatively charged, and which, from their positions about the nucleus, neutralize the positive charges on it. The electrons are arranged in a definite configuration about the nucleus of each atom. They are not of necessity held absolutely still. There is no reason why they may not move about, but the area of activity of each electron that forms a part of an atom is circumscribed within limits of space similar to that of its neighbor. Unlike the nuclei which, as we have just said, are held to be peculiar to each element, we consider the electrons to be all alike.

Now let us bear in mind the atomic numbers of the elements in the order of their atomic weights in the periodic table. They are: H, 1; He, 2; Li, 3; Be, 4; B, 5; C, 6; N, 7; O, 8; F, 9; Ne, 10; Na, 11; Mg, 12; Al, 13; Si, 14; P, 15; S, 16; Cl, 17; Ar, 18; K, 19; Ca, 20; Sc, 21; Ti, 22; V, 23; Cr, 24; Mn, 25; Fe, 26; Co, 27; Ni, 28; Cu, 29; Zn, 30; through to U, 92.

ATOMIC NUMBER COINCIDES WITH ELECTRO-POSITIVE CHARGES.

Thanks to the brilliant Moseley of Manchester, England, killed as a private soldier in the flower of his youth in the Gallipoli fight, we have confirmation of the statement that the atomic number of each element in the periodic table and the number of electro-positive charges on the nucleus of its atom are the same. Thus from the above we read that the number of positive charges on the nucleus of the hydrogen atom is 1; that of the lithium atom is 3; carbon, 6; nitrogen, 7, and so on, so that the table of atomic numbers is also that of the positive charges on the nucleus of the atom of each element. From this we gather also that the nucleus of the atoms of no two elements can be the same, and we learn, too, that the table of atomic numbers gives, in addition to the foregoing, the number of electrons that are attached to, and form part of, every atom of every element. There must be an electron to neutralize every positive charge, because the difference between an atom and an ion is that in the former every positive charge of the nucleus is satisfied with an electron, and is therefore neutral, while in an ion this is not the case. In an ion there are either more or fewer electrons than will completely balance the positive charge of the nucleus of the atom, or the nuclei of the atoms, which constitute it.

In acknowledging and accepting in part certain theories of W. Kossel and G. N. Lewis, Dr. Langmuir carries them further, with various changes and extensions, but, as already stated, for the sake of brevity we shall not attempt to indicate the specific authorship of each idea.

III

By themselves electrons repel each other, but in the presence of positive charges they show a disposition to arrange themselves into definite groups; they indicate a law, or series of laws, of configuration, and this is the first step in the present work. If, then, these groupings, these configurations, may be found complete in the most stable of the elements, and incomplete in others, we may infer that in the inert gases the electrons are satisfied, that they have fulfilled their tendency to conform to certain arrangements, and that the activity of other elements is due to the drive to conform as nearly as possible to the complete, and therefore inert, elements. The author of these postulates will have nothing to do with metaphysics in the development of his theories of the constitution of atoms and molecules, but we cannot resist the observation that in this pair-forming and octet-forming nature of electrons about positive charges we find suggested the tendency in nature toward a condition of balance and rest which is the basis of the great postulate of Gautama Buddha, and the substance of the ancient philosophy of the East.

HELIUM THE MOST STABLE ELEMENT.

Different elements do not behave the same; they differ in their nuclei and in their arrangement and number of electrons, but in this striving to become as nearly as possible like the fixed gases we find the

*From *Ohm and Metall Engineering* (New York).

key to all chemical phenomena. It behooves us, therefore, first to consider the most stable element, which is helium. The atomic number of helium being 2, the positive charge of its nucleus is 2, and it has two electrons. How are these arranged? There being but two they cannot follow an isometric system: the simplest would be the tetragonal system, having, like the earth, a polar axis and an equatorial plane (Postulate I). We imagine these two electrons as held by the positive charges of the nucleus very much as though the nucleus were in the center and the electrons each in the half of a complete shell, say, like a walnut-shell, that surrounds it. Neither electron crosses the plane which divides these two hemispherical shells. We might picture, as in Fig. 1, a cross section of the helium atom, cut a little above the equator, so as to show all charges, the positively charged nucleus indicated by ++ and each of the electrons by a — sign.

IV

This must be the most permanent arrangement of electrons about a nucleus: one electron in each half of a spherical shell, and neither trespassing upon the territory of the other. And while there is no reason to regard the electrons as stationary, save that each keeps within what we call its cell, it will be convenient for us to consider each as occupying its average position, which would be on an axis perpendicular to the plane which divides them. Here we have a complete satisfaction of the positive and negative charges with almost no force extending beyond the atom in any direction. Let us say the electrons have achieved a position of complete balance and contentment, thus making helium the most permanent substance known. Because there is practically no external force about the atoms, and the primary disposition of its electrons to form pairs is satisfied, the atoms do not form molecules; they remain independent and inert. So independent and inert are they that not only is He a gas, owing to the lack of external force about its atoms, but these atoms are readily separated, and its boiling point is therefore only $4\frac{1}{2}$ degrees above absolute zero. We have, then, in helium, the achievement of the first electronic ideal: the grouping in pairs about a positive charge. Such a central part we consider to be common to all atoms except that of hydrogen: the nuclei varying from 2 to 92 positive charges, according to the element, and the first pair of electrons invariably next to the nucleus.

V

The next element to helium in point of stability is neon. Its atomic number being 10, we must find an ideal arrangement of its ten electrons. The nucleus has ten positive charges, and the conclusion is that the first pair group themselves about the nucleus, just as in helium, leaving eight positive charges to be satisfied. These eight electrons arrange themselves in a second shell outside that containing the pair, four in either hemisphere of the outer shell, and each in its own cell. A top view would appear as in Fig. 2, with the nucleus and pair hidden under the outer shell. A perspective view would be as in Fig. 3. These eight electrons, four in either hemisphere of the outer shell, we call an octet. This shell is twice the diameter of that including the pair below it, and its surface is four times as great. This is in order to give the same space or room to each cell. There are eight cells, and every cell in the outer shell of neon is occupied. Now since we hold that chemical activity emanates mainly from the outer shell of electrons, there is no occasion for chemical activity in neon. And bearing in mind this greater chemical activity of the outermost shell we shall follow G. N. Lewis in calling all that part of any atom that is within the outer shell, its *kernel*. The second disposition of electrons is to group themselves into octets, and here they have done it. We have a pair, and an octet, all balanced, all filling every available space, and so there is no chemical activity to neon. It is inert; it is a gas; it has a low boiling-point, and it does not form molecules. It is completely satisfied as it is, and next to helium it is the most stable element. The next element in order of stability is argon, atomic number 18. This is just like neon, except that, according to Postulate IV, each cell of the second shell contains 2 electrons, making 2 in the first and 16 in the outer shell. This is also a permanent gas. In krypton, atomic number 36, we have two in the first shell, 8 + 8 in the second, and have 18 still to dispose of. The third shell will contain 18 electrons; 9 in each hemisphere. One of these 9 electrons will go to the pole, and the remaining 8 will be distributed symmetrically about it. The same thing happens in the other

hemisphere. With xenon we have krypton as the kernel (except that the nucleus has 18 more positive charges) and the 18 more electrons are distributed in the same manner in the third shell, making 2 in each cell, and including one more in a cell at each pole. Niton follows as the last, with 32 electrons in the fourth shell, 16 in each hemisphere.

In other words, we assume these inert and stable elements to be made up of successive and consecutive groups of electrons about the nucleus of each, consisting of first the nucleus, next a pair of electrons, and then consecutive octets and double octets with a pair in the polar position whenever there is an odd number of electrons to be provided for in each hemisphere. According to Postulate IV, all inner shells must have their full quota of electrons before the outer shell can contain any, but we note that in the inert elements the outside shells have their full quotas also. *This is the very reason for the stability and inactivity of these elements;* the electrons are ideally placed, they are electrically balanced, there is a minimum field of external force about the outer shells, therefore they all are gases, and have low boiling points.

No element other than the inert gases has its outer shell satisfied, i. e., every cell of its outer shell occupied, and therefore the electrons in the outer shell are always striving to make pairs of octets with some other electrons. *This is the basis of all chemical combination and reaction.* We shall try to make this more evident as we proceed.

VI

When we consider hydrogen, atomic number 1, we have but a single charge and a single electron. We have not even a pair. The lone electron is ever trying to form a pair, and therefore the atoms pair off in molecules. Note, please, in Postulate VI that a stable pair may be held by two hydrogen nuclei. Of course the hydrogen molecule is not as stable as an inert gas but compared with a single hydrogen atom which

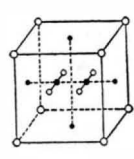


FIG. 4

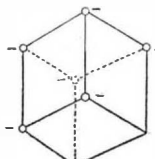
Nitrogen
Molecule

FIG. 5

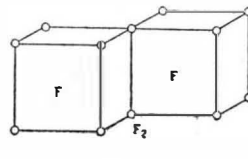
Fluorine Atom (5) and
Molecule (6)

FIG. 6

has an exceedingly short time factor for its separate existence, the hydrogen molecule is very stable. It has the lowest boiling point of all substances except He, being but 20 deg. absolute. Due to such complete saturation within itself its external force is slight, and it shows slight chemical activity until it is split up into atoms. The old *status nascendi* theory in regard to hydrogen worked well in that it referred really to unpaired hydrogen atoms. If we take from a hydrogen atom its single electron we have left of course the hydrogen ion.

Lithium with its atomic number of 3 has three electrons, of which two form a pair about its nucleus and which constitute the lithium ion, while the third is easily detached, because it tends to form pairs or octets. We read in Postulate VI that the two atomic kernels can very rarely hold a pair of electrons as is the case with the H molecule. The lithium kernel already has its pair, and therefore it cannot get another nucleus into its kernel. The lithium atom with but one electron in its second shell produces a strong electrostatic field which extends into surrounding space. There being no free nuclei about which the single outside electrons can group themselves into pairs or octets, it is electrostatic force which holds the atoms together, a second upon the first, a third upon the second, a fourth upon the third, and so on, *ad infinitum*, so that it appears to build itself into a solid lattice work structure. Therefore it is a solid. It melts and boils with difficulty. Because of the free electrons it is a good metallic conductor, but for lack of enough available electrons to form octets on the outer shell it has no tendency to form molecules either in a solid, liquid or gaseous state.

PROPERTIES OF FLUORINE IN THE LIGHT OF THE THEORY.

Fluorine has the atomic number 9, or one less than neon, so that it has a pair about the nucleus and seven in its outer shell, lacking but one electron to make the octet complete. The cumulative effect of its seven outside electrons to form an octet is so great as to give it intense chemical activity. If brought into

contact with lithium it takes the electron from it and completes its octet, making the fluorine ion negatively charged, and leaving the lithium ion positive. Let us repeat this to make it clear. Fluorine has nine positive charges on its nucleus, and about it is, first, a pair of electrons, and then seven more in its outer shell. With seven electrons all placed in a shell with eight cells, and all seven trying to form an octet, the effort is likely to be intense. And it is. Nobody ever called fluorine inert! That lone extra electron of lithium in an outer shell (although, of course, the concept of shells and cells is a concept of space only) is pulled over to the vacant space in the fluorine outer shell. That leaves the lithium ion free. But with nine positive charges on the nucleus of fluorine and ten electrons now engaged, the fluorine ion becomes negatively charged because of ten electrons about its nucleus with + charge of 9. So too the lithium ion, which has a triple positive charge on its nucleus and has lost an electron, has now but two instead of three negative charges, which makes the lithium ion positive. The force, however, which holds this ion to the fluorine ion with its octet of electrons is electrostatic; there is no opportunity for pairs of electrons to be held in common by the two elements, therefore there is no LiF molecule. Every lithium ion is attracted to all the negative fluorine ions about it, and *vice versa*, so that it builds up a lattice work of the two ions, as in Bragg's salts. It is a solid, but it is a non-conductor, because there are no free electrons, every octet being satisfied. If, however, we melt it, then it becomes an electrolytic conductor, because the ions are then free to move around.

RELATIVE CHEMICAL ACTIVITY OF HALOGENS.

Here is an illuminating note which explains why the halogens decrease in chemical activity as they increase in atomic weight, and therefore in atomic number, while with the alkali metals the opposite is the case. Not only does fluorine stand next to neon, but all the halogens stand next to the inert gases, each having one electron less. Chlorine bears this relation to argon, bromine to krypton, and iodine to xenon. But as these inert gases increase in atomic number they become less stable, as is indicated by their decreasing ionization potentials and their increasing boiling points. There is greater distance or greater interruption between the positively charged nucleus and the negatively charged electrons in the outer shell as atomic numbers increase. Therefore it stands to reason, among the halogens, that as they increase in atomic number their electro-negative qualities decrease in intensity. On the other hand lithium stands next to helium, and the other alkaline metals bear a similar relation to the inert gases, each having one electron more rather than one less, as with the halogens. This lone electron on the outer shell is given up in the presence of a positive charge; it cannot well draw on seven other electrons to complete the octet. But the electrostatic force between the nucleus and the outermost electron becomes less and less as the kernel grows larger and larger, because the distance between the positively charged nucleus and the outermost electron becomes greater. Therefore the outermost electron becomes more readily detachable as the size of the atom increases, so that sodium is more electro-positive than lithium, while potassium is more electro-positive than sodium.

Carbon, atomic number 6. Here the atom is composed of a pair of electrons about the nucleus, and four in the outer shell. By virtue of the larger charge in the kernel these are not easily given up, as in lithium, but may be regarded as constantly trying to draw on four more electrons to make up an octet. The atom is symmetrical, and its tetravalency is persistent. Its well balanced but incomplete structure explains both its permanency in combination and its high boiling point.

(To be continued)

Graphic Ammeters

The modern graphic ammeter is lighter, cheaper and more easily used than semi-portable graphic wattmeters, and, although the latter are more accurate, the graphic ammeter is sufficiently accurate for many industrial purposes. A graphic ammeter connected in a motor circuit shows at what time the motor was started and stopped; and also gives the power consumption at no-load and when loaded. The instrument also shows the number of operations performed by the machine driven and whether the machine is being operated correctly and at maximum production. —Abstracted by *The Technical Review* from *Power* (New York).