Molecule Formation as a Question of Atomic Structure

W. KOSSEL
Annalen der Physik 49, 229-362 (1916).

The periodicity of behavior which previously had been considered as the most important characteristic of the series of elements and the basis of all studies of atomic structure has been pushed strongly into the background by the results obtained in recent years. Since Lenard's discovery that cathode ray absorption follows mass, it has been discovered for the first time that there is a unity of matter to ward electrical phenomena, and the number of such facts has constantly grown, until finally the laws of Rontgen ray spectra have established in the clearest manner that among the elements there is a continuous series of structures of the same type, in which the identical type of alterations of dimensions occurs from step to step. Therefore there have been more and more studies which approach a concept of treating chemical behavior so that only the constituents of this unitary building material are everywhere involved and all ad hoc assumptions of special types are avoided; in this view the periodic phenomena reflect only an alteration in the order of the outermost of the constituents mentioned. The present work is devoted to this theme, since it considers the question of how simple may be the major features of molecule formation that can be described, and what assumptions will be necessarily required.

The result is that remarkably few special assumptions are necessary at first for a description of the basic facts that can give the behavior of compounds that have polar characteristics. Since the overwhelming majority of the compounds of inorganic chemistry of a wide variety of elements have a polar character, there is a corresponding reduction in the number of compounds of special, individual elements that must at first have specific assumptions, and thus need special treatment. Such compounds lie among the homopolar compounds of other elements, especially in the realm of carbon compounds, concerning which Stark's special picture of electron arrangements has already given such outstanding results, and where the special requirements are obviously already beginning to be worked out in the structure of the diamond.

Basic Assumptions. In what follows we will not use any of the previous proposals as expressed in individual atomic models; rather we will employ only such general assumptions as seem to be experimentally well grounded. We will therefore naturally begin with well-known ideas.

We envisage the method of molecule formation as the coming together of the electron structures of different atoms. We will thus generalize the ideas which Helmholz in his time developed concerning electrical elementary quanta. In electrolytic dissociation we are acquainted with separation of molecules in which the number of elementary quanta agrees with the number of valence units passed from one component to the other, as chemical experience shows. Since the freely moving elementary quantum is known to have only a negative charge, the exchange of charges will occur especially here; the passing of an electron will be assumed, while the positive charge, whose structure for the moment will be left open, remains in the mass of the atom. The number of available electrons in the atom and the conditions under which it is possible for them to leave the atom will be the factors that determine the chemical behavior of the atom. As to what first sets the total number of electrons in the atom, we accept van den Broek's hypothesis that makes this equal to the order number of the elements in the periodic table. This assumption seems necessary to satisfy the results of the studies on Rontgen ray scattering and especially the exact results that have been obtained for the relative number of electrons from the interaction of various kinds of atoms in interference in crystals; we assume that a more accurate formulation of the theory, which today is somewhat incomplete, will not bring about any very fundamental changes in the results. Since as it seems, never more than eight valence units are active in an atom, in most cases we must deal with the exchange of only a small portion of the electrons present, and so the question arises, how to consider the order of the electrons in the atom so as to understand why only a definitely determined number of them can enter into an exchange. It is generally accepted, to be sure, that the, electrostatic forces and the electromagnetic forces that they overcome are modified for all the electrons of an atom by the approach of another atom. Experience has already shown, however. that this action, as judged from the emission frequencies, is of a completely different order of magnitude for different electrons. We are forced to assume that the conditions by which the frequency is determined for some of the electrons of a heavy atom entering a molecular union are altered only very slightly,

while for others (emitting the "optical frequencies") the conditions are fundamentally changed. It is required as much from the valence properties as from emission that each element must have a determined atomic structure whose various electrons are approachable from the outside and able to be affected in different degree. The simplest picture is given when we assign to the interior of the atom those electrons that are not affected and whose high frequency in any case is related to some sort of strong binding (quasielastic or quantum holding), while the valence electrons and those active at optical frequencies are more loosely bound and can be affected; these are considered to be lying on the surface of the atoms.

On the basis that we have reviewed, we thus conceive of the valence properties as an expression of the behavior of the outermost electrons of the atom, and henceforth we will follow them through a series of elements from below upwards.

According to the van den Broek assumption, each successive element will contain one more electron and one more elementary quantity of positive charge than the previous one. This is primarily shown by the fact of the periodic changes of the valence number so that as the elements pass from lower to higher weight the configuration is not altered uniformly (also perhaps not if the newly arriving electrons are assumed to add on singly to the structure already formed arranged on a spiral). In the course of a regular change we are much more likely to come to a configuration in which the number of electrons capable of valence activity is repeated, and also some in which practically no tendency to exchange exists, the noble gases, among others. In order to come closer to the assumption now becoming necessary, we will at first confine ourselves to the region of the two short periods and the beginning of the first long one; the region from He to Ti. Here, after eight element positions there is repetition of the same chemical properties and the same valence maxima. After addition of eight electrons, we once more get the same surface order for the atoms. The continuity with which the K frequency in the whole periodic system depends on the unit number (the number of the element in the periodic system) shows that the periodicity found in the sequence in no way extends to the whole electron structure, but is limited to the surface. Accordingly, we can follow up the simplest idea that suggests itself: the order of the inner electrons remains unchanged in the elements that follow each other, always similar in each element and only changing its size through the continuous increase of the charge, which corresponds to the same increase in characteristic frequencies. The electrons that come anew in the sequence of atomic weights will always add to the outside and their order will be such that the observed periodicity results from the fact of their approach from outside. This leads to the suggestion that these electrons that are newly added are arranged in concentric rings, or shells, in which (perhaps because of conditions of stability that we will not discuss) only a definite number of electrons, here eight, can find places. If a ring or shell is completed, the next element must begin a new one; the number of electrons approaching entirely from outside again increases from element to element and thus the chemical character is repeated by building a new shell.

In order to test these ideas more fully, we now ask in which column of the periodic table we must seek the elements in which a new shell from some electron lying outside is begun. This can be seen from strictly chemical considerations. The characteristic of the alkali metals always to give up electrons with great ease-for example, to show greater "emissivity" for electrons when there is more violent heat motion in the surroundings-suggests to us that in them an electron is bound especially loosely and is exposed to outside influences; this suggests that in the area of the periodic system discussed above we can consider, on the basis of experimental evidence, that Na and K are elements in which, outside the completed shell, the first electron of the new shell is located. To the preceding elements Ne and Ar we must then logically ascribe an atomic structure in which a shell or a ring of electrons is completely closed, while the preceding Fl and Cl lack one electron in theirs. Now we know that these last, the halogens, are elements that whenever possible seek to acquire electrons: they have, we might say, "a high affinity for free electrons." It appears, then, that the configuration of the outer electrons reached in the noble gases can be considered somewhat analogous to an equilibrium state. Not only do the noble gases themselves lack an inclination, to take up electrons ("no affinity for free electrons") or to give them up ('they have the highest splitting tension yet measured), but also the neighboring configurations endeavor, by giving up or taking on electrons, to form systems of the same total number of electrons as the noble gases. The configurations they form are thus not only exceptionally stable themselves, resisting all changes, but also are the prototypes of the configurations that the neighboring systems, which have only a slightly different normal number of electrons or few different positive charges, form preferentially by electron exchange with the

surroundings. In the picture of the arrangement of shells that we will finally use we will assume as the most natural idea that the foreign electron in a halogen atom thus serves to close an almost completed shell.

On the basis of the behavior of the elements adjacent to the noble gases, we will proceed further experimentally. On the one hand, we assume that throughout an atom those electrons that lie outside the last completed shell are given up considerably more easily than those which belong to it. On the other hand, we assume that generally atoms whose number of electrons approaches that of a noble gas (the completion of a shell) have a tendency to add as many foreign electrons as will give the "stable" form of the noble gas. Since the number of electrons of the neutral atom agrees with the position in the sequence of atomic weights (reported as already known in part from the Rontgen ray spectra), we find that the number of electrons that can be taken up or given off also has a simple relation to this position. To the halogens, which stand immediately before the noble gases, we ascribe the ability to bind *one* electron; the elements of the preceding sixth column of the system, O and S, for example, must correspondingly take up two electrons to reach the number of a noble gas, the next preceding N and P must take up three, and so on. The tendency for such addition seems to decrease with increasing distance from the noble gases. On the other side of the noble gases we find analogously the opposite function of the atoms; the most electropositive, most easily losing electron elements are the alkali metals; they are followed with decreasing tendency to give up electrons by the alkaline earths, which already have two more electrons than the noble gases. Consequently here we go through a series: the elements of column III, B and Al, have three electrons that easily separate; those of column IV, four; those of VII, seven; until finally in the eighth element, the next noble gas, the new ring is closed. Obviously we agree completely here with Drude's results, which showed that the number of loosely bound electrons which give dispersion agrees excellently with the Abegg valence theory provided we indicate each possible valence position as a detachable electron. We now turn to a consideration of the evidence from valence. In the physical processes on which we based our previous considerations we obviously only very rarely considered such a great accumulation as would correspond to maximum loss of electrons by the halogens. We now must show that the electron exchange which leads to chemical molecule formation is as useful for our expanded picture.

Molecule Formation. Up to this time we have generally considered electron exchange of the individual atoms with their surroundings; now we will consider the consequences when more atom systems (at least two) are brought together, when we find that they have opposite tendencies in the exchange process. For instance, if a halogen atom comes together with an alkali metal atom, we find for both atoms the opportunity for the tendency that they follow as free atoms: the alkali metal gives up the farthest outlying electron, as in a flame, and the halogen takes it up to close its ring. Both now adhere to each other electrostatically, since the halogen system as a whole is negatively charged, and the alkali positively charged. These charges appear separately if the molecule is brought into a medium of high dielectric constant so that the electrostatic attractive force is weakened. If it becomes too slight to maintain an equilibrium under the shock of thermal agitation, the system separates in terms of its present situation: the halogen retains its abnormal electron as an anion, the alkali metal shows an excess of positive charge. Both have completely lost the chemical properties that they show as neutral atoms, since they have satisfied their characteristic tendencies. This fact is necessarily connected with their structures. The fact that perhaps a potassium ion does not behave in water like a neutral potassium atom, that a solution of chloride does not show the properties of a water solution of chlorine gas, always occurs because here the atoms are charged, which must basically change their properties. This change follows directly from the fact that the atoms have given up their characteristic activities of reaction. This behavior necessarily follows: the K^+ ion has completely lost its specific chemical activity with the loss of the cause of this activity, the outer electron; the Cl^- ion has obtained what it otherwise always tends to acquire; both reach their structures because of these directing and attracting forces and the tendency to electron exchange of these elements. We will return later to ion formation (Part II); here we have elucidated the manner of chemical bonding by the ideas we have introduced and further expanded. The two atoms that are bound as a result of passage of their elementary charges have been monovalent, and polar in two different ways: the halogen attracts one electron into its system to build a stable configuration; the alkali metal gives one up readily. It is essential for our theory that in processes like this, as we often find today, each valence position as seen chemically has a "valence electron" arranged on the atom, but the specific negative valence position, that on the halogen in our case, is perhaps to be considered as a "free place" with respect to the element following in the periodic system, which the atom strives to fill up. We continue with the cases which at least are similar and which occur in the overwhelming majority of inorganic compounds

where there is necessary a polarity of function shown in the atoms as valence; this reminds us of the experimental material which Abegg obtained from his comprehensive study from the purely chemical side and which has likewise interpreted valence as a polar function.