XXXIII.—*Atomic and Molecular Numbers.*

By Herbert Stanley Allen.

Atomic Numbers.

Atomic weight and its determination have occupied a prominent position in the work of chemists since Dalton first put forward the Atomic Theory. Recent investigations in connexion with radio-

active elements and lead derived from radioactive substances have proved that the atomic weight has not the unique value hitherto attributed to it, and that a chemical element, such as lead, may be a mixture of "isotopes" occupying the same place in the periodic classification, but inseparable by chemical methods. Increasing importance is now being attached to the atomic number of an element, that is, the number which denotes the position of the element in Mendeléev's periodic table. As is well known, there are a few instances in which the place of the element is not in agreement with the atomic weight determinations; in such cases, the atomic number is given the value appropriate to the place in the table assigned by the chemical or physical properties. The values of the atomic numbers now accepted are given in table I, which follows the periodic classification of the elements commonly adopted. A better representation of the facts is obtained by employing a spiral in three dimensions. In this case, hydrogen may be placed at the pole of the spiral.

According to the electrical theory of matter, the atom consists of a central nucleus or core, carrying a resultant positive charge, surrounded by rings of negative electrons. It was first suggested by van den Broek that the number of the place in the periodic table was the same as the number of electrons in the atom or the number of unit charges carried by the nucleus. The same suggestion was made shortly afterwards by Soddy in connexion with the radioactive changes in the last thirteen places in the periodic table. The hypothesis is confirmed by the measurements of Barkla on the intensity of the X-radiation scattered from various substances. These indicate 7 electrons per atom of N, 8 for O, 6 for C, 16 for S, 1 for H. Rutherford's work on the scattering of α-particles by atoms of matter led him to the conclusion that the concentrated nuclear charge was approximately equal to half the atomic weight multiplied by the charge of an electron. The atomic numbers are, in fact, roughly equal to half the atomic weight.

It was, however, through the work of Moseley on the frequency of vibration of the X-rays, which are characteristic of the elements, that the importance of the atomic numbers was firmly established. The square root of the frequency of a line in the X-ray spectrum was found to be proportional to a number which increased by unity in passing from one element to the next in the periodic table. Thus every element from aluminium to gold may be characterised by an integer, N, which determines its X-ray spectrum. These atomic numbers were tabulated for the elements in question on the assumption that N for aluminium is 13. Between uranium and hydrogen, only five places remain vacant. For the rare earths,

PERIODIC SYSTEM OF THE ELEMENTS.

O	I	II	III	IV	V	VI	VII	VIII
	H 1							
He 2	**Li 3**	**Gl 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	
A* 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	Ga 31	Ge 32	As 33	Se 34	Br 35	
Kr 36	Rb 37	Sr 38	Yt 39	Zr 40	Cb 41	Mo 42	—43	Ru 44 Rh 45 Pd 46
	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te* 52	I* 53	
Xe 54	Cs 55	Ba 56	The 57— Rare Earths					
					Ta 73	W 74	- 75	Os 76 Ir 77 Pt 78
	Au 79	Hg 80	Tl 81	Pb 82	Bi 83			
Nt 86		Ra 88		Th 90		U 92		

* Elements not placed in the order of the atomic weights.

which have not been tabulated in table I, Moseley found the following values for N: La, 57; Ce, 58; Pr, 59; Nd, 60; Sa, 62; Eu, 63; Gd, 64; Ho, 66; Er, 68.

It may now be regarded as certain that most of the properties of the elements depend on the value of the atomic number rather than on that of the atomic weight. For example, the atomic frequency which determines the thermal behaviour of the element in the solid state has been shown by the author (*Proc. Roy. Soc.*, 1917, [*A*], **94**, 100; *Phil. Mag.*, 1917, [vi], **34**, 478, 488) to bear a simple relation to the atomic number. Certain electronic frequencies are related to the atomic number in a similar way.

It will be noticed that Moseley's work does not give an unique determination of the value of N, since it is based on the assumption that N is 13 for aluminium. Rydberg has suggested that two unknown elements should be included in the periodic table between hydrogen and lithium, so that the atomic number of lithium would be 5 instead of 3. For all the elements later in the table, Rydberg's ordinals would be greater than Moseley's numbers by 2 units. Evidence in favour of Moseley's numbers is accumulating. Thus Barkla's results on the scattering of *X*-rays by air show that the number of electrons is as near to 7 for an atom of nitrogen as it is possible to estimate the pressure of the air under which the experiments were made. In the work of the present author on the relation between atomic frequency and atomic number, it was found that the atomic numbers of Moseley gave more satisfactory agreement than did the atomic ordinals of Rydberg. The same conclusion was arrived at by van den Broek (*Phil. Mag.*, 1914, [vi], **28**, 630).

The atomic numbers express in a compact form many facts that have been long familiar to students of chemistry. They afford a striking confirmation of the statement of Chancourtois, made in 1863: "The properties of the bodies (elements) are the properties of number." Newlands assigned to the elements numbers (from 1 to 56) to indicate the order in which the elements must be placed when arranged in the ascending order of their atomic weights. He put forward the "law of octaves," according to which the numbers for members of the same family will differ by 7, or some multiple of 7, provided that the elements are not consecutive. Newlands admitted that it might be necessary to alter the number (7) separating analogous elements to some higher figure should a large number of new elements be discovered (compare Garrett, "The Periodic Law," 1909, Ch. III.). An examination of the atomic numbers of table I shows that in many cases the difference between the numbers for members of the same family is either 8

or some multiple of 8. In other cases, however, the difference is found to be 18. Thus in the case of the inert gases of the zero group, the atomic numbers for He (2), Ne (10), A (18) show differences of 8, whilst A (18), Kr (36), and Xe (54) show differences of 18. The interval between Xe (54) and Nt (86) is $32 = 4 \times 8$. In the case of subsidiary families of the same group, a common difference of 10 is manifest, for example, K (19), Cu (29), or Rb (37), Ag (47). The reason for these variations from the more commonly observed difference of 8 is the presence of three elements (for example, Fe, Co, Ni) instead of a single element in Group VIII of the table. The two extra elements change the common difference from 8 to 10 or from 16 to 18. Thus the law of octaves must be replaced by a new rule, which may perhaps be termed the rule of eight—a rule, however, to which there are quite definite exceptions (1) in the consecutive elements of Group VIII, (2) in the elements displaced two units by Group VIII, (3) in the metals of the rare earths.

Molecular Numbers.

The author has suggested the introduction of the term "molecular number" to signify the sum of the positive charges carried by the atomic nuclei contained in the molecule. Thus the molecular number bears the same relation to the atomic number as the molecular weight bears to the atomic weight. When a molecule contains a atoms of an element A, b atoms of B, and c atoms of C, its chemical formula may be written $A_aB_bC_c$, whilst its molecular number will be $N = aN_a + bN_b + cN_c$, where N_a, N_b, N_c are the atomic numbers of the component elements. For example, the molecular number of water (H_2O, hydrol) is 10, for the molecule contains two atoms of hydrogen (nuclear charge, 1) and one atom of oxygen (nuclear charge, 8). Thus the C.G.S. system of units is a decimal system in a deeper and more intimate sense than its originators supposed, for it is based on the assumption that the gram is the mass of 1 c.c. of water at the temperature at which its density is a maximum. This fact probably accounts for the remarkable numerical relations, involving powers of 10, which the author has shown to exist between certain fundamental physical constants (*Proc. Physical Soc. London*, 1915, **27**, 425).

The four compounds, CH_4, NH_3, H_2O, HF, formed by the combination of hydrogen with a "typical" element belonging to successive groups in the second series of the periodic table, all have the same molecular number, 10. The corresponding elements in the third series of the table form compounds with hydrogen of the

same type, SiH_4, PH_3, H_2S, HCl, all having the molecular number 18 (=10+8).

It may be remarked here that the molecular number is usually, but not invariably, an even number. This arises from the fact that when the valency is odd, the atomic number is usually odd also; but in the case of an element, such as copper, which may be either univalent or bivalent, or in the case of some of the metals of Group VIII the molecular number may be odd.

We have seen that the atomic numbers of analogous elements usually differ by 8 or a multiple of 8, or in some cases by a number that is 2 units greater than one of the foregoing. It is obvious that results of a similar character are to be expected in dealing with the molecular numbers of analogous compounds. The halogen compounds of the alkali metals may be considered by way of illustration. The results are collected in table II, the figures in italics being the differences between the molecular numbers in adjoining rows or columns.

TABLE II.

Element.	F 9 Fluoride.		Cl 17 Chloride.		Br 35 Bromide.		I 53 Iodide.
Li 3	12	*8*	20	*18*	38	*18*	56
	8		*8*		*8*		*8*
Na 11	20	*8*	28	*18*	46	*18*	64
	8		*8*		*8*		*8*
K 19	28	*8*	36	*18*	54	*18*	72
	18		*18*		*18*		*18*
Rb 37	46	*8*	54	*18*	72	*18*	90
	18		*18*		*18*		*18*
Cs 55	64	*8*	72	*18*	90	*18*	108

The molecular number of a cuprous haloid exceeds by 10 that of the corresponding potassium compound, and similarly the molecular number of a silver haloid exceeds by 10 that of the corresponding rubidium compound.

In the case of an element which has a valency greater than 1, the results may be more complicated, since one or more of the atomic numbers may require multiplication by a numerical factor depending on the number of atoms in the molecule. For compounds containing only elements from N=1 to N=25, however, comparatively simple results will be obtained, since the divergences due to the three elements in Group VIII do not then appear.

Instead of the law of octaves, we have what has been termed the rule of eight holding, with certain exceptions, in connexion with the molecular numbers of analogous compounds.

The value of N for a compound radicle can be calculated in the same way as for a complete molecule. Thus for the ammonium group (NH_4), the value of N, which may be called the group

number or the radicle number, is 11. It is noteworthy that this is the same as the atomic number of sodium, which can be replaced by the ammonium group in so many of its compounds. The principle here involved may be extended, and we may say that in a chemical compound one radicle may frequently be replaced by another having the same number, or a number differing from the first by 8 or a multiple of 8.

The hydrogen molecule, H—H (N = 2), may be regarded as the typical simple molecule, from which a large number of chemical compounds may be derived by substituting for one or both of the hydrogen atoms another atom or radicle.

Thus water may be looked on as a typical compound in which one atom of hydrogen (N = 1) is combined with the hydroxyl group, OH (N = 9). The hydroxyl group may be replaced by CH_3, NH_2, F, for each of which N = 9, giving rise to the compounds methane, ammonia, and hydrogen fluoride. Again, in each of these compounds the hydrogen atom may be replaced by one of the groups mentioned, giving rise to such compounds as C_2H_6, $CH_3{\cdot}OH$, N_2H_4, $NH_2{\cdot}OH$, H_2O_2, for which the molecular number is $9+9=18$.

Owing to the fact that the group number of $\cdot CH_2\cdot$ is 8, the rule of eight is prominent in the case of organic compounds. In open-chain compounds, the addition of each CH_2-group means an increase of 8 in the molecular number.

It is necessary to enter a caution as regards the interpretation of the results when dealing with a chemical group or radicle. The "group number" may be taken to represent the sum of the charges of the atomic nuclei of the group. It will only represent the number of negative electrons associated with the radicle as well when the radicle, considered as a whole, is not charged or electrically neutral. According to the views of Sir J. J. Thomson (*Phil. Mag.*, 1914, [vi], **27**, 768), the radicle may be charged either positively or negatively, and in such a case the number of negative electrons will differ from the radicle number here given.

The molecular numbers here discussed, and the relations between them, are not mere arithmetical curiosities. It is to be remembered that the molecular number is associated with a perfectly definite physical conception, namely, the number of unit charges found in the positive nuclei of the atoms in the molecule or the number of the complementary negative electrons. It is to be anticipated that the molecular numbers will play an important part in determining the physical or chemical characteristics of molecules or radicles. Some progress, in fact, has already been made in establishing such a connexion. It has been shown by Nernst and others that the thermal behaviour of a compound in

the solid state depends on a certain characteristic frequency or frequencies. The author has found (*Phil. Mag.*, 1918, [vi], **35**, 338) that simple relations exist between the products obtained by multiplying such a frequency and the molecular number of the compound. Thus there must be an intimate connexion between the specific heat and the molecular number. In the author's opinion, it is safe to predict that other physical properties of chemical compounds will be found to depend on the values of the molecular numbers.

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