ART. XXII.—*Remarks on the Atomic Weights of the Elements;* by WOLCOTT GIBBS, M.D., Prof. of Chemistry and Physics in the Free Academy in New York.

IN the present communication I shall endeavor to show that if the atomic weights of oxygen, sulphur and carbon are taken, respectively, as 16, 32 and 12, those of a majority of the other elements must be doubled. I do not at present adopt the view in question; my object is simply to point out the logical consistency of the change. For the sake of convenience and precision of language I shall employ the terms atom, molecule and equivalent, in the sense in which they are understood by the chemists of the new or unitary school.* An atom of any element is the least quantity of that element which can exist in combination: a molecule is the least quantity which can exist in the free state. The definitions of atomic and molecular weights flow at once from those of atom and molecule. The equivalents of bodies are the relative quantities which replace each other in actual or ideal substitutions; they may correspond to atoms or to molecules, or may bear a simple numerical relation to either of these. The atomic weights of carbon, oxygen and sulphur are now generally considered to be respectively 12, 16 and 32, chiefly upon the following grounds:

1. In all volatile organic compounds the constitution of which has been accurately determined, the number of atoms of these elements is always even, if we consider the weights of the atoms to be respectively 6, 8 and 16. Provided that all such compounds are assumed to correspond to 2 vols. of vapor (H=1).

2. Purely chemical considerations appear to show that in organic compounds, independently of any assumption as to vapor-volumes, the number of atoms of carbon, oxygen and sulphur is always even.

3. When oxygen or sulphur replace hydrogen in organic compounds, 2 units of weight of hydrogen are replaced by 16 of oxygen or 32 of sulphur; 4 units of hydrogen by 32 of oxygen, and so on; in no case is one unit of weight of hydrogen replaced by 8 of oxygen.

4. The least quantity of oxygen or sulphur set free in any reaction is either 32 or 64, or is some multiple of 32 or 64. In like manner the least quantity of oxygen or sulphur which reacts with any compound body is a multiple of 16 or 32 by an even number.

The assumption is now generally made that the molecules of all substances in the gaseous state occupy the same volume:

* See for example Kekulé, Lehrbuch der Organischen Chemie, i, 97, Erlangen, 1859.

from this it follows that in the greater number of cases two atoms unite to form one gaseous molecule. The difficulty which formerly existed in the case of sulphur has been completely removed by the researches of Deville and Troost, and of Bineau, who have shown that the volume occupied by 16 parts of sulphur in the form of perfect gas is $\frac{1}{2}$, and not $\frac{1}{3}$ of that occupied by 1 part by weight of hydrogen. In the case of those substances the vapor-densities of which correspond to *four* volumes, it appears probable that decomposition into two 2-volume molecules occurs, so that the observed vapor-densities are the sums of the densities of the constituent molecules. Thus sal-ammoniac* in the form of vapor is HCl and NH_3, these constituents recombining at a lower temperatute to NH_4Cl. In this manner, among others Kopp† and Hofmann‡ have shown that it is unnecessary to admit the existence of 3-volume, 4-volume and 6-volume vapors. There exists however at least one exception to the law now generally admitted that, in the case of the elements, one molecule consists of two associated atoms. The vapor-density of phosphorus, even at a temperature of 1040° C., corresponds to $\frac{1}{2}$ vol., the atomic weight being taken as 31. Since sulphur, which is less volatile than phosphorus, is a perfect gas even at 860°, we cannot admit that the case is otherwise with phosphorus, or reasonably suppose that the vapor-density would correspond to one volume if determined at a still higher temperature. We must therefore admit that the molecule of phosphorus corresponding to 2 vols. of vapor contains 4 atoms, and not 2 like that of nitrogen, while nothing is more certain than that the atomic weights of phosphorus and nitrogen are respectively 31 and 14. In like manner the vapor-density of arsenic appears also to correspond to $\frac{1}{2}$ volume only, though it has not yet been determined at temperatures very far above the boiling point.

If now we admit that the molecules of all substances occupy 2 vols. in the gaseous state, and if the reasoning which has led chemists to double the old atomic weights of carbon, oxygen, sulphur, &c., be correct, it follows that the atomic weights of the greater number of the elements must be doubled. For we find:—

1. That nearly all volatile inorganic oxyds, chlorids, oxychlorids &c. contain in 2 vols. of vapor (H=1) two or four received equivalents of metal or radical. Thus the compounds whose formulas are now usually written $SiCl_2$, $TiCl_2$, ZCl_2, $SnCl_2$,

* Deville and Troost have shown that sal-ammoniac corresponds to 4 vols. of vapor even at a temperature of 1040° C. At this temperature ammonia must be resolved into its elements, and its vapor-density ought to correspond to 6 vols. instead of 4. The explanation in the text is therefore not applicable to all cases. Comptes Rendus, xlix, 239.

† Ann. Chemie und Pharmacie, cv, 390.

‡ Comptes Rendus, xlix, 781.

$HgCl$, Hg_2Cl, $HgBr$, Hg_2Br_2, Fe_2Cl_3, Al_2Cl_3, Al_2I_3, Al_2Br_3, CrO_2Cl, must be written Si_2Cl_4, Ti_2Cl_4, Z_2Cl_4, Sn_2Cl_4, Hg_2Cl_2, Hg_4Cl_2, Hg_2Br_2, Hg_2I_2, Fe_4Cl_6, Al_4Cl_6, Al_4I_6, Al_4Br_6, $Cr_2O_4Cl_2$, in order to correspond to 2 vols. of vapor.

2. All volatile metals and metallic oxyds contain two or four received equivalents in 2 vols. of vapor. Thus the vapor-densities of mercury and cadmium represent the molecular weights Hg_2 and Cd_2. Arsenous and osmic acids correspond in the form of vapor to the formulas As_2O_6 and Os_2O_8.

3. All volatile compounds of metals with organic radicals contain an even number of equivalents of metal in 2 vols. of vapor, excepting only those in which triatomic metals occur. Thus we have corresponding to 2 vols. of vapor the formulas:—

$$\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}Zn_2,\quad \left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}Zn_2,\quad \left\{C_2H_3\right\}_4Sn_2,\quad \left\{C_4H_5\right\}_4Sn_2,$$

$$\left.\begin{matrix}(C_2H_3)_2\\(C_4H_5)_2\end{matrix}\right\}Sn_2,\quad \left.\begin{matrix}(C_4H_5)_2\\Cl_2\end{matrix}\right\}Sn_2,\quad \left.\begin{matrix}(C_4H_5)_2\\Br_2\end{matrix}\right\}Sn_2,\quad \left.\begin{matrix}(C_4H_5)_3\\Br\end{matrix}\right\}Sn_2,$$

$$\left.\begin{matrix}(C_4H_5)_3\\Cl\end{matrix}\right\}Sn_2.$$

4. The volatile compounds of the triatomic radicals, nitrogen, phosphorus, arsenic, antimony, bismuth and boron, contain in 2 vols. of vapor only one received atomic weight of the radical. Thus we have the compounds:—

NH_3, PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$, BCl_3, $P(C_4H_5)_3$, $As(C_4H_5)_3$, $Sb(C_4H_5)_3$, $B(C_4H_5)_3$, $BO_3\ 3C_4H_5O$, &c. &c.

To this there are exceptions. Thus we have corresponding to 2 vols. the formulas:—

$$As_2O_6,\quad \left.\begin{matrix}(C_2H_3)_2\\(C_2H_3)_2\end{matrix}\right\}As_2,\quad \left.\begin{matrix}(C_2H_3)_2\\(C_2H_3)_2\end{matrix}\right\}As_2O_2,\quad \left.\begin{matrix}(C_2H_3)_2\\(C_2H_3)_2\end{matrix}\right\}As_2S_2.$$

5. The specific heats of the atoms of nearly all the elements are equal if the molecule is in each case referred to 2 vols. of vapor.*

If now we consider it proved from the above considerations that the molecular weights of carbon, silicon, tin, titanium and zirconium, correspond in the gaseous form to 2 vols., and that these elements are tetratomic, it follows from analogy that certain other elements are also tetratomic, and we have the group:—

Carbon,	12	1·68	Lead,	208	6·52
Silicon,	28	—	Palladium,	108	6·40
Zirconium,	44	—	Rhodium,	102	5·62
Titanium,	48	—	Ruthenium,	106	—
Niobium,	96	—	Platinum,	198	6·40
Tantalum,	136	—	Iridium,	196	7·00
Tin,	116	6·52	Osmium,	194	5·92

* The only exception to this law occurs in the case of carbon, and cannot at present be explained.

The first column of numbers giving the atomic weights, the second the atomic heats or the products of the atomic weights into the specific heats. It is possible that thorium belongs to the tetratomic group, as thoria appears to be ismorphous with stannic acid, Sn_2O_4. Lead is placed in this group from the analogy of the compounds which it forms with ethyl, methyl, &c. to stannethyl, &c.: it appears however like tin, palladium, ruthenium, platinum, rhodium, iridium and osmium to be also diatomic; the so-called protoxyds having the formulas Pb_2O_2, Sn_2O_2, &c. For similar reasons we admit the existence of 6 triatomic elements, namely:—

Nitrogen,	14	—	Antimony,	120	6·11
Phosphorus,	31	5·85	Bismuth,	208	6·41
Arsenic,	75	6·10	Boron,	11	—

The diatomic elements, according to the reasoning above mentioned, will be 30 in number, and may be arranged in natural families, as follows:—

Oxygen,	16	—	Iron,	56	6·38
Sulphur,	32	6·48	Manganese,	54	—
Selenium,	80	6·08	Cobalt,	60	6·42
Tellurium,	128	6·08	Nickel,	58	6·28
———			Chromium,	52	—
Magnesium,	24	—	Aluminum,	27·5	5·88
Calcium,	40	—	Zinc,	65	6·24
Strontium,	88	—	Cadmium,	112	6·36
Barium,	136	—	Copper.	63	6·04
———			Uranium,	120	—
Cerium,	92	—	Mercury,	200	6·40
Lanthanum,	94	—	———		
Didymium,	96	—	Molybdenum,	96	6·91
Yttrium,	—	—	Tungsten,	184	6·67
Erbium,	—	—	Vanadium, ?	138	—
Terbium,	—	—	———		
Glucinum,	10	—			
Thorium, ?	118	—			

This classification into natural families appears to me to represent the present state of our knowledge, though the position of several elements must be regarded as doubtful.* The monatomic elements are only 10 in number; they may be arranged in three groups:

Chlorine,	35·5	—	Hydrogen,	1	—	Silver,	108	6·16
Bromine,	80	–6·74	Lithium,	7	—	Gold,	197	6·38
Iodine,	127	6·88	Sodium,	23	6·71			
Fluorine,	19	—	Potassium,	39	6·60			

* There is reason to believe that vanadium belongs with boron to the nitrogen group.

It is however to be remarked that, of the other elements, at least two, namely copper and mercury, are monatomic in certain combinations, as for example, in Cu_2Cl and Hg_2Cl. It is true that we may write these formulas Cu_4Cl_2 and Hg_4Cl_2, in which case we have two additional diatomic forms of copper and mercury with the atomic weights 126 and 400 respectively. This mode of viewing the subject obliges us to admit atomic heats represented nearly by the number 12, or twice as high as in the case of the other elements, and appears therefore less simple than that first stated.

In like manner all the elements belonging to the tetratomic group which form protoxyds, &c., may be regarded as tetratomic and diatomic; this will add at least eight to the number of diatomic elements. Finally, in the sesquioxyds and similar compounds two received atoms of iron, manganese, chromium, aluminum, &c., must be regarded as forming a single triatomic atom. Limpricht* and Frankland† admit the existence of pentatomic elements, including the nitrogen group in this class, but this view is not generally adopted, and in the present state of our knowledge a primary division of the 60 elements into four classes, the monatomic, diatomic, triatomic and tetratomic elements, appears to be sufficient.

From the above it appears that of the 60 elements now known to chemists, the received atomic weights of 50 at least must be doubled, if we admit the correctness of the reasoning which has led many chemists at the present day to double the atomic weights of carbon, oxygen and sulphur. Wanklyn‡ and Wurtz§ have already suggested the propriety of doubling the equivalents of zinc and tin, and by analogy, of several other metals, while Cannizzaro‖ has adduced the specific heats of the atoms with other arguments in favor of the same change. Wurtz compares oxyd of zinc Zn_2O_2, with oxyd of ethylene $(C_4H_4)O_2$; the hydrate of oxyd of zinc will then correspond to glycol, $\left.\begin{matrix}Zn_2\\H_2\end{matrix}\right\}O_4$. In the same way we may consider hydrate of sesquioxyd of iron as corresponding to glycerine, $\left.\begin{matrix}\overset{\prime\prime\prime}{Fe_2}\\H_3\end{matrix}\right\}O_6$ to $\left.\begin{matrix}\overset{\prime\prime\prime}{C_6H_5}\\H_3\end{matrix}\right\}O_6$, Fe_2 being here triatomic.

Should the further progress of the science show that the views above mentioned are the most simple and consistent expression

* Limpricht. Lehrbuch der Organischen Chemie, 1te Abth., 8.

† Quarterly Journal of the Chemical Society, vol. xiii, Nos. 2 and 3.

‡ The same, vol. xiii, p. 124.

§ Ann. de Chimie et de Physique, lx, 239, and Repertoire de Chimie pure, ii, 405.

‖ Il nuovo Cimento, vii, 321. I have not seen the original paper and quote at second hand from the Jahresbericht of Kopp and Will for 1858, p. 12.

of all the facts, it will be desirable to return to the notation of Berzelius slightly modified, that is to say, it will be better to halve the atomic weights of hydrogen and the other monatomic and triatomic elements, and denote the atomic weights of carbon, oxygen, sulphur, zinc, &c., by the numbers 6, 8, 16, 32,5, &c., respectively. In this manner while the formulas are written with precisely the notation of the new school, the numbers actually employed in the great majority of calculations will be those which have been sanctioned by longest usage, and which are most convenient for practical purposes. The atomic weights of hydrogen, chlorine, potassium, and the other monatomic elements, will be in each case one half of the old equivalent, while the molecular weights will correspond with the old equivalents. Thus we shall have:—

Hydrogen,	½	1	Oxygen,	8	16
Chlorine,	17·75	35·5	Carbon,	6	12
Bromine,	40	80	Zinc,	32·5	65
Potassium,	19·5	39	Iron,	28	56
Nitrogen,	7	14	&c. &c.		

in which table the first column gives the atomic and the second the molecular weights.

The formula of water thus becomes H_2O and its atomic weight 9; caustic potash is $\left.\begin{matrix}K\\H\end{matrix}\right\}O$ and its atomic weight 28; oxyd of zinc will be ZnO and its atomic weight 40·5; chlorhydric acid will be HCl and its atomic weight 18·25. The dashed symbols ~~H~~, ~~Cl~~, ~~K~~, &c., may also be employed, as in the Berzelian notation and would in many cases be extremely convenient.

All the typical formulas now so generally employed will be written as at present, the actual weights only being changed. The general acceptance of the views of the new school would be greatly facilitated by the adoption of the system of atomic weights here proposed.

In another paper I propose to discuss the question of the basicity of the elements with other points of special theoretical interest.

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