Fourth Liversidge Lecture.

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By FRANCIS WILLIAM ASTON, Sc.D., F.R.S.

Physical Atomic Weights.

ATOMIC weights are an old subject in Chemistry. The combining ratios of the elements were being determined to 1% a hundred years ago by Berzelius and other distinguished chemists. Purely physical methods of measuring atomic weights are, on the other hand, quite modern, they have indeed only just attained their majority. By " physical atomic weights " I do not mean those which are obtained by measuring the densities of gases. The actual measurements may in this case be called physical, but for them to be of any value the gases must be pure and purification is of all laboratory operations the most essentially chemical.

The title of my lecture refers to results obtained by comparing the actual weights of individual atoms, not, as in the older methods, the mean weights of countless myriads. Such operations were first shown to be practicable by Sir J. J. Thomson in 1910 when by improved technique of his famous " parabola " method of positive ray analysis he obtained sharp parabolic streaks with hydrogen which could only be given by streams of atoms having essentially equal masses. It cannot be too much emphasised that this was the first experimental proof of Dalton's postulate that atoms of the same element had the same weight; until then this had been purely an article of faith, one of the most valuable ever held, for upon it modern chemistry was built. Now the building is secure we may knock away the old scaffolding, since, as you all know, Dalton's postulate has been proved wrong for almost every element in existence.

All the early results with the parabola method appeared to support Dalton's simple chemistry. In the cases of such gases as hydrogen, nitrogen, oxygen and carbon monoxide the masses of the atoms and molecules compared appeared in exactly the positions expected from the chemical atomic weights, for the measurements could only be made with an accuracy of about 1% and it so happens that those of all the elements concerned are integral to within that margin.

When neon was introduced two parabolas appeared, a strong one at 20 and a weak one at 22. The atomic weight of neon determined by its density was 20·20, so this result suggested that neon had

atoms whose masses differed by two units. This was in fact the starting point of the work on the isotopes of the inactive elements. In order to prove the isotopic constitution of neon greater accuracy of analysis was necessary, and this was obtained by means of the first mass-spectrograph set up in 1919. By this apparatus one could compare masses with an accuracy of 1 in 1000 and now for the first time it was possible to check the chemist's values with a precision comparable with that of his analysis.

The first results again were in excellent agreement. Not only did the masses of oxygen, carbon, helium and nitrogen, assumed to be simple elements, agree with accepted values, but the isotopes of the complex elements neon, chlorine and argon were found to obey the "whole number rule" and, from a rough estimate of the relative intensity of their lines, appeared to be present in the proportion expected from their chemical atomic weights. Of still greater interest was the discovery that the mass of the hydrogen atom when compared with helium and oxygen by the special device of "bracketing" was not a whole number but corresponded with the well-established chemical value 1·008.

The first serious discrepancy was noted in the case of krypton, which gave a group of six lines corresponding to masses definitely integral, but when the position of the centre of gravity of this group was estimated it gave a value for the mean atomic weight of 83·5 $\pm$ 0·3. The accepted international figure deduced from the density was 82·92. On the other hand the relative intensities of the boron lines 10 and 11 suggested a value less than the chemical one, 10·90, then in use. Xenon when analysed gave an estimated mean weight 131·3 $\pm$ 0·3 (intl. 130·2), showing a discrepancy similar to that of krypton. The most glaring case was antimony, which gave two lines of almost equal strength 121, 123, whereas the chemical value 120·2 was still in use. The chemical figure 9·1 for beryllium was not in agreement with the positive ray evidence that this was essentially a simple element. Revision of the chemical atomic weights reduced to small values the discrepancies in the cases of boron, beryllium and antimony, but those of krypton and xenon remained.

In all these cases the relative abundance of the isotopes was estimated visually from the appearance of the lines on their mass-spectra. The first actual measurements of relative abundances were made by Dempster in 1921 by analysing positive rays magnetically and comparing the currents carried by the isotopes by an ionisation method. Dempster did not determine the masses of the isotopes, but by assuming the whole-number rule he was able to show that the isotopic constitutions of magnesium, potassium,

calcium, and zinc were in fair accord with their chemical atomic weights.

A further advance in accuracy was made by the construction in 1925 of the second mass-spectrograph. This was designed to measure the variations from the whole-number rule and under favourable conditions could compare masses with an accuracy of 1 in 10,000. These variations, called " packing fractions," have been determined for the principal isotopes of some 33 elements up to date, that of the standard atom of oxygen 16 being taken as zero. When plotted against mass-numbers, the packing fractions of all but the light elements appear to lie approximately on a smooth curve which descends in the region of mass-number 50 to a maximum negative value of -10 parts per 10,000 and then rises again, crossing the zero line in the region of mercury 200.

If its packing fraction is known, the mass of any species of atom, now generally called its " isotopic weight," can be at once written down on the physical scale $O^{16} = 16$. When the first results for packing fractions were published in the Bakerian Lecture of 1927 oxygen was still supposed to be a simple element, in which case this scale and the chemist's scale $O = 16$ would be identical. But in 1929 Giauque and Johnson showed by the analysis of optical absorption bands that O^{17} and O^{18} were also present. The quantities of these isotopes are so small that confirmation by the mass-spectrograph has been difficult, but this has now been done and the line 32 has been photographed with satellites 33 and 34 due to $O^{16}O^{17}$ and $O^{16}O^{18}$ respectively. The abundance of 17 and 18 is still uncertain, 1 in 3000 and 1 in 600 being approximate figures, so that the chemical unit would be about 2 parts in 10,000 heavier than the physical one. We can now write down the atomic weights on the chemical scale of elements essentially simple, such as iodine, and the agreement in most cases is well within 0.1%.

The majority of elements are, however, complex, so that in order to determine the mean atomic weight some means of measuring the relative abundance of the isotopes must be found. About four years ago I worked out a method of doing this by the photometry of mass-spectra. The original object of these researches was to see if any simple numerical relations were to be found. As is well known there are no such relations between the abundances of elements on the earth, nor would they be expected owing to the practical difficulty of sampling, for they are segregated by all sorts of natural processes. On the other hand, since the discovery of isotopes hundreds of analyses have been made to test the unvarying nature of the atomic weights of naturally occurring complex elements, and, with the possible exception of boron, all have given

consistently negative results. Only in the laboratory has variation been achieved, and that with extreme difficulty. We may therefore say briefly that, whereas it is impossible to obtain a mixture of elements which we may regard as a fair sample of cosmic matter, it is very nearly as impossible to obtain a mixture of isotopes which is *not* a fair sample of a complex element. The hope of simple relations was admittedly small. It has not been realised, but on the other hand data have been obtained which may prove of great value in formulating theories of the evolution of the elements and have enabled the atomic weights of a number of complex elements to be determined.

One great difficulty with the photometry of mass-spectra is that the source is never reproducible and seldom constant for more than a very short time. Another is that the relation between abundance and blackening of the plate is completely different for different elements.

For the preliminary work krypton was taken as the most suitable standard element. It has six isotopes with a good range of abundance, which are easy to resolve. It works well in the ordinary vacuum discharge and when mass rays are produced in this way it is perfectly safe to assume that the proportion of the isotopes in the beam will be absolutely invariable. The measurement of the fundamental ratio between the abundances of the two strongest isotopes 84 and 86 was made by a method which virtually eliminates photometric error and may be called the method of intermittent exposures. By means of a mechanical contact maker carrying two arms and rotating once in 15 seconds the lines were photographed with normal and with reduced times of exposure, the two images being kept clear of each other by a small change of the potential applied to the electric deflecting field. The effect of this change of potential on the intensity will in any case be small and was actually eliminated, as far as possible, by taking a second picture with the shift reversed. The breaking up of one long exposure into a great many short ones ensures a minimum effect from continuous change in the intensity of the source. The ratio of the exposures was altered by changing the angle between the arms of the contact maker until the reduced image of the stronger of the two lines and the normal one of the weaker were virtually equal. The ratio for exact equality could now be calculated and when this had been corrected for the effect of the penumbra of the neighbouring lines and for the relative positions of the two lines on the plate the value 3·41 for the relative abundance of Kr 84 compared with Kr 86 was obtained. This was probably within 2 or 3% of the true value.

The same procedure enabled the ratios of abundance of other

isotopes to be ascertained. The difficulties and inaccuracies increase in the case of the fainter lines, but on the other hand the relative effect on the value of the mean atomic weight becomes less at the same time. The following figures were found for the percentage abundances of the isotopes of krypton :

78	80	82	83	84	86
0·42	2·45	11·79	11·79	56·85	16·70

These figures give a " mean mass number " of 83·857. This, corrected for the mean packing fraction of — 8·8 in 10,000, gives the atomic weight on the physical mass scale $O^{16} = 16$ as 83·783. Correcting to the chemical scale, we get 83·767, a value agreeing well enough with the first estimate from its mass-spectrum but much higher than the international value 82·92 in use at the time these measurements were made.

The experience gained with krypton was of great value in extending the work to other elements. With heavy elements such as mercury it is impossible to apply the method of intermittent exposures, since the resolving power of the apparatus does not permit the photography of a line between two others without overlapping. In such cases a large number of short exposures of different periods were employed and the best mean values adopted from the curves so obtained. Once the values for mercury had been definitely ascertained it was possible to use its group as a convenient standard reference scale for other heavy elements such as osmium and tungsten.

As a method of determining atomic weights photometry of mass-spectra is clearly at its worst for light elements, for its error will be roughly a fixed fraction of the unit of mass. In addition, with isotopes so different in mass as those of lithium it is obviously unsafe to conclude that particles of the same energy will affect the photographic plate equally. In the region of mercury and lead, however, the three sources of uncertainty due to errors in packing fraction, change of scale, and relative abundance, respectively, have each about the same probable error, namely, about 1 part in 10,000. Here the method compares well with the best chemical practice and has obvious advantages from the fact that purity, in general, is of no importance and the quantity of material usually required is only a fraction of a milligram. In the accompanying table are given the best ascertained physical results, corrected by a factor of 2 in 10,000 to the chemical scale, together with the latest international values for comparison.

It will be seen that the agreement in the great majority of cases is exceedingly satisfactory.

Table of Chemical and Physical Atomic Weights.

Element.	Atomic number.	International atomic weight.	Physical atomic weight.	Element.	Atomic number.	International atomic weight.	Physical atomic weight.
H	1	1·0078	1·00761	Sr	38	87·63	87·64
He	2	4·002	4·00136	Nb	41	93·3	92·90
Li	3	6·940	6·936	Mo	42	96·0	95·97
B	5	10·82	10·803	Ru	44	101·7	(101·1)
C	6	12·00	12·0037	Sn	50	118·70	118·71
N	7	14·008	14·008	Sb	51	121·76	121·78
O	8	16·000	16·000	Te	52	127·5	127·58
F	9	19·00	18·996	I	53	126·932	126·91
P	15	31·02	30·98	Xe	54	131·3	131·26
Sc	21	45·10	44·96	Cs	55	132·81	132·91
Cr	24	52·01	52·01	Ba	56	137·36	137·42
Zn	30	65·38	65·33	Ta	73	181·4	180·89
Ge	32	72·60	72·65	W	74	184·0	183·96
As	33	74·93	74·92	Re	75	186·31	186·22
Se	34	79·2	78·96	Os	76	190·8	190·31
Br	35	79·916	79·911	Hg	80	200·61	200·62
Kr	36	83·7	83·767	Tl	81	204·39	204·41
Rb	37	85·44	85·43	Pb	82	207·22	207·19

The case of hydrogen is particularly interesting. The discrepancy was less than 1 in 5000 and for my own part I was content to ascribe it to experimental error. If so, it is a lucky error, for it lead Urey and his colleagues to search for heavier isotopes in hydrogen. An isotope of mass number 2 has now been definitely identified, but the most reliable data show that it is only present to the extent of 1 part in 35,000, an amount quite inadequate to account for the discrepancy which led to its discovery.

The physical value for boron is probably low on account of the enhanced photographic effect of its lighter isotope. Scandium, niobium, and tantalum are shown by their mass spectra to be essentially simple and there seems little doubt that their chemical atomic weights are too high. The same is true, but to a less degree, of phosphorus and cæsium. The first physical value for zinc was identical with the chemical one, but Bainbridge has since shown that hydrides were present. The effect of these has now been taken into account, but the peculiar unsymmetrical distribution of abundance in the zinc isotopes will tend to give a large photographic error and the corrected result given in the table is probably too low.

The serious difference in the case of selenium has now been removed by Hönigschmid, who in his latest revision gets a value identical with the physical one. The first value for tellurium was obtained under difficulties and now a much better mass-spectrum analysis has been achieved by Bainbridge, who discovered three new light isotopes. The corrected and the chemical value are now in good agreement. Support of the high value for krypton has led

to the international figure being raised. The latest density determinations made by Whytlaw Gray on xenon with a micro-balance give a value, 131·26, identical with that obtained by the photometry of its mass-spectrum. On the other hand the physical value for osmium makes it difficult to accept the figure 191·55 recently suggested by Gilchrist. Data for uranium are of great interest. Contrary to expectations its mass-spectrum shows it to be at least 97% 238. It has not yet been possible to measure its packing fraction, but it appears very improbable for it to have a positive value high enough to agree with the present chemical atomic weight 238·14.

In conclusion I should like to urge the need of further research. Although the discovery of isotopes has admittedly robbed the chemical atomic weights of some of their fundamental interest, I sincerely hope work on them will be continued by both purely chemical and purely physical methods. It is of vital importance that the values for all elements used in chemical reactions should be known *with certainty* to within one part in a thousand. If discrepancies occur, they must be removed. If in a particular case this cannot be done, so much the better—a discrepancy in the density of nitrogen which obstinately refused to be removed was the cause of the discovery of argon, from which proceeded the most important advance in inorganic chemistry in living memory.