

ATOMIC WEIGHTS AND ISOTOPES¹

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The idea that all forms of matter must be composed of finite invisible particles is older than authentic history: a crude atomistic hypothesis was unquestionably one of the earliest attempts of thinking man to explain his environment. Three thousand years ago the highly civilized Egyptians, indeed, seem to have found no need for this doctrine. So far as we can ascertain from their writings and tombs, they were chiefly concerned with practical questions; but perhaps their cumbersome hieroglyphics were inadequate to transmit more subtle thoughts. However this may have been, there can be no question that their contemporaries, the dreamers of India and Asia Minor, were often devoted to considerations of an abstract type. The possibly independent origins of the Vaiśeshika philosophy and the atomistic theories of the legendary Leucippus, of his vigorous disciple, Democritus, master of common sense, and of their followers in the Epicurean and Lucretian schools, are veiled in the mists of antiquity.

How deeply Newton, who was a firmly convinced atomist, may have penetrated into an understanding of the material side of things, no one can tell. The evidence was irretrievably lost by the burning of his precious manuscripts, the content of which he would never after divulge. As all the world knows, the plausible dream first became a practical chemical tool when Dalton showed, only one hundred and twenty years ago, that a definite atomic hypothesis forms the most reasonable explanation of the constant and multiple combining proportions of the elements, discovered by himself (1). That substances should

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combine chemically with each other in this fashion is obviously best explained by the assumption that the chemical combining proportions are determined by the weights of the respective atoms concerned. The outcome is a remarkable instance of the development of a vague philosophical dream into a highly practical and extraordinarily useful tool for coördinating and advancing concrete knowledge.

About twenty-seven years ago, the discovery of radioactivity brought at first much perplexity into the well established and superlatively helpful chemical atomic doctrine. Few discoveries of isolated facts have produced a greater upheaval in scientific thought. One of the consequences of the new knowledge was a revival of a belief of the medieval alchemists, namely, their belief that the transmutation of the elements might be possible. Indeed, whether or not the common elements may ever be transmuted into each other in weighable quantities, at least there can be little question that radium, for example, a well-defined chemical element of the calcium group, disintegrates spontaneously, producing helium and a form of lead. If then a well-defined "chemical element" can disintegrate, if its atoms can split into pieces, what becomes of the atomic theory, which had been for over a century the chief basis of chemical reasoning? Has one a right to retain any longer the old definitions of the words "element" and "atom"? Moreover, what significance can the relative weights of the atoms possess? For the atoms were previously supposed to be truly indivisible, and the elementary substances composed of them were imagined to be the ultimate constituents of the Universe. These questions are far-reaching in their influence on chemical thought.

From time to time it is well, as regards any field of human activity, to review existing knowledge, revise one's premises, and endeavor to ascertain to what extent one's former views are still valid. The surprising outcomes of the last quarter of a century make such a revision of the subject of atomic weights particularly opportune at present.

As a matter of fact, we find that the knowledge of thirty years ago is still, for the most part, intact. The only two

assumptions no longer tenable are: first, that the elements are absolutely permanent and necessarily incapable of transmutation or decomposition; and second, that all the atoms of a given element possess always exactly the same weight. Both of these assumptions must today be abandoned; but they are seen on close scrutiny to be by no means the essential part of the chemical atomic theory. They were merely a priori postulates of philosophical hypothesis. Doubt has indeed been cast upon both of them even in the decades preceding the discovery of radium.

As long ago as 1815 an English physician named Prout (2) had advanced the belief that all heavier atoms are simply aggregations of atoms of hydrogen. The fortunes of this hypothesis will be discussed in the sequel. Astrophysicists have more than once suggested that the high temperatures and violent electrical environment of the sun and stars might disintegrate all our earthly elements into this gas. Chemists also were open-minded on the subject, in spite of the failure of the alchemists. For example, twenty-five years ago I attempted to disintegrate the atoms of metals by means of Trowbridge's unique storage battery of very high electromotive force, with negative results. Thus the doctrine of transmutation had been seen to be a reasonable possibility, but remained unconfirmed. On the other hand, as regards the second assumption, again and again investigators of atomic weights had thought that they had discovered dissimilarity in the weights of atoms of a given element, only to discover later that the conclusion was the result of inadequate care in experimentation. Thus the two revolutionary ideas were not new; the revolution came only when definite incontrovertible evidence had been produced in their support. Indeed, as I have implied, these ideas, revolutionary as they are, are rather an extension of our knowledge than an overthrow of previously discovered truth. All the common elementary substances which are concerned in everyday life are just as permanent and just as definite as ever, under ordinary conditions. All the chemical reactions upon which life depends and which we have used in industry or research are unchanged.

The chemical atomic theory employed for explaining these reactions, and the quantitative relations which the reactions exhibit, are entrenched today far more firmly than they were thirty years ago. Avogadro's Rule (3), upon which the symbolic notation of chemistry has long rested, has a validity much more convincing than Avogadro himself could ever have imagined.

Our more recently acquired knowledge involves primarily the discovery of facts which throw light on the nature and the possible structure of the interior of the atoms. The study is pursued with the new conviction that the atomic structure is not quite so stable as we formerly believed it to be. The "hard, massy particle" of Lucretius and Newton is now believed to be a conglomeration neither infinitely hard nor wholly indestructible. The modification of ancient doctrine is based chiefly upon the study of extreme and highly unusual conditions; nevertheless, the new knowledge is of profound interest, not only as regards these extreme conditions, but also because of the light which it may throw upon the stable fundamental conditions pertaining to everyday phenomena.

We find that for the ordinary purposes of chemistry, the atomic weights in particular have lost little of their fundamental significance. They have indeed acquired a new significance, and the field of research into their exact values has been widened rather than contracted. For if, as we now believe, some at least, of the elements are capable of disintegrating, we must find not only the weights of the original "atoms" which have belied their ancient title, but also those of the fragments into which they split. Moreover, if, as will be discussed more fully in the sequel, a given element may have atoms of somewhat different weights, it appears that these weights are not a matter of chance or accident, but are rather determined inevitably by the internal structure of the atoms and the circumstances of their evolution. Accordingly, with many elements we have not one atomic weight, but rather two or more, to determine, in order fully to understand the nature of the substances concerned. Modern discovery thus substantiates a statement made over fifteen years ago:

The question as to whether or not the supposed constants of physical chemistry are really not constants, but are variable within small limits, is of profound interest and of vital importance to the science of chemistry and to natural philosophy in general. If this latter alternative is true, the circumstances accompanying each possible variation must be determined with the utmost precision in order to detect the ultimate reason for its existence. As Democritus said long ago, "The word chance is only an expression of human ignorance." No student of natural science who perceives the dominance of law in the physical universe would be willing to believe that such variation in a fundamental number could be purely accidental. Every variation must have a cause, and that cause must be one of profound effect throughout the physical universe. Thus the idea that the supposed constants may possibly be variable instead of invariable, adds to the interest which one may reasonably take in their accurate determination, and enlarges the possible field of investigation instead of contracting it (4).

These considerations being indubitable, let us now briefly review the more important bearings of atomic weights today, discussing at first the methods of determining these quantities, and afterwards some of the more important significations of the results.

METHODS OF DETERMINING ATOMIC WEIGHTS

Three methods of quite different nature and theoretical bearing are chiefly used today for the determining of atomic weights. The first of these methods, which must still be considered the more generally convenient, is that involving the chemical analysis of pure substances. Thus may be determined the proportions by weight in which elements combine with one another.

To this classical method, used in the first place by Dalton and later by Berzelius, de Marignac, Stas and a host of others, has been added, more recently, two other radically different methods. One of them, that which involves the comparison of the molecular weights of gases, based upon Avogadro's Rule, has only within the last thirty years received much credence, because only recently has Avogadro's Rule been believed to be an exact generalization. That is to say, only recently have

the deviations from the law of perfect gases exhibited by the actually imperfect gases, whose densities are to be compared, been understood.

Finally there is a third method, of very few years standing, namely, the method devised by J. J. Thomson (5), and greatly improved by F. W. Aston (6), which depends upon measuring the inertia of single charged atoms or molecules as deflected by an electric (and magnetic) field. This last method enables us to appraise with considerable approximation the weights of selected groups of individual atoms, and thus furnishes highly important evidence concerning the proposition that different atoms of the same element may have different weights.

Let us review these three methods in succession. The exact determination of atomic weights by each of them rests upon precise laboratory work; in each, peculiar precautions are needed.

What, now, are the most important precautions to be taken in quantitative chemical analysis, in order to attain the greatest precision? In the first place, each portion of substance to be weighed must be free from the suspicion of containing unheeded impurities; otherwise its weight will mean little. This is an end not easily attained. In the next place, after an analysis has once begun, every trace of each substance to be weighed must be collected and find its way in due course to the balance. In brief, "the whole truth and nothing but the truth" is the aim. The chemical side of the question is far more intricate and uncertain than the physical operation of weighing. Every substance must be assumed to be impure, every reaction must be assumed to be incomplete, every measurement must be assumed to contain error, until proof can be obtained.

All the chemical world knows very well how faithfully and earnestly Berzelius, de Marignac and Stas labored toward the attainment of perfection in this problem, using highly refined quantitative methods (7). Each added to the successful outcome of those before him, and in turn each provided invaluable experience for his followers. Modern exactness could not have been attained without the preliminary preparation afforded by their labors, and all honor is due them. The execution of exact

quantitative analysis is a laborious, nerve-taxing, and time-consuming performance, and nothing but a firm conviction of the importance and significance of the outcome can give patience and courage for its prosecution. As Tyndall said:

Those who are unacquainted with the details of scientific investigation have no idea of the amount of labor expended in the determination of those numbers on which important calculations or inferences depend. They have no idea of the patience shown by a Berzelius in determining atomic weights; by a Regnault in determining coefficients of expansion; or by a Joule in determining the mechanical equivalent of heat. There is a morality brought to bear upon such matters which, in point of severity, is probably without a parallel in any other domain of intellectual action. The desire for anything but the truth must be absolutely annihilated; and to attain perfect accuracy no labor must be shirked, no difficulty ignored (8).

In spite of all Stas's pains devoted to the subject, even he did not attain the highest possible accuracy. In the course of recent years it has gradually developed that his values for the metals were all somewhat too high (9). The errors resulted from a variety of small imperfections which happened to tend for the most part in one direction. Perhaps the most serious of these faults was due to the fact that Stas used such large quantities of material that he could not prepare his substances with the requisite degree of purity, and could not conduct his analyses of the huge portions of substances employed under the best conditions. The result was that his silver, which was used as a standard of reference, contained impurity, as Dumas suspected long ago. The standard of reference for metals being somewhat too high, all the computed results for metals were too high also. Another error tending in the same direction was due to the fact that because of his precipitation of his preparations in concentrated solutions, the precipitates contained adsorbed or occluded impurities. This error was avoided in more recent work by the use of more dilute solutions. These special precautions, namely, the avoidance of occlusion and adsorption, are among the most important of those which must be heeded in such work. Of equal importance are the elimination of unrecognized water,

and the avoidance of error in estimating minute amounts of substances in solution. Among yet others should be enumerated the danger of loss by evaporation, and the danger of contamination from the vessels employed. Modern physical chemistry has greatly assisted in recent work, by pointing out possible dangers and offering prescriptions for their avoidance. The scope of the present article does not permit of full discussion of such details, but a few words may be devoted to two among the disturbing circumstances, for the correction of which new devices have been used during the last thirty years.

Among all the possibilities of error, the unsuspected presence of water is perhaps the most frequent and most insidious. In recent times forms of apparatus have been devised, which enable one to dry, enclose, and weigh an anhydrous substance in such a manner as to preclude the admission of a trace of water from the atmosphere. They might well find applications in every quantitative laboratory (10).

Another instrument which likewise has greatly facilitated recent work is called the "nephelometer" (11). With the nephelometer, minute traces of suspended precipitate may be approximately determined from the brightness of the light they reflect. Traces of substance, which are too attenuated to be caught on any ordinary filter, may thus be estimated. This instrument also has developed wide usefulness.

The two errors obviated by these simple devices—namely, the presence of residual water and the loss of traces of precipitate, respectively—have perhaps ruined more previous investigations than any other two causes.

As an example of the methods employed, a recent investigation which had as its object the simultaneous determination of the atomic weights of lithium, silver and chlorine in relation to oxygen, may be briefly described (12). A new method was involved, namely, the determination of the quantitative relations of lithium chloride to silver on the one hand and to the oxygen of the corresponding amount of perchlorate on the other hand. It is evident that by dividing one of these ratios by the other

the relation of silver to four atoms of oxygen will be obtained. Expressed algebraically:

$$\frac{\text{Ag}}{\text{LiCl}} \times \frac{\text{LiCl}}{\text{LiClO}_4 - \text{LiCl}} = \frac{\text{Ag}}{\text{O}_4}$$

Thus the problem resolved itself into discovering just how much silver is needed to precipitate a known weight of lithium chloride on the one hand and how much oxygen must be added to a known weight of lithium chloride in order to convert it wholly into perchlorate on the other hand. The accuracy of the solution of these quantitative problems depended upon the following essentials:

First, the lithium chloride which should serve as the starting-point must be wholly pure—free not only from other metals and non-metals in the form of salts, but also from moisture and from dissolved gases.

Second, the amount of silver equivalent to this lithium chloride must be determined by precipitating the chlorine in a known amount of the lithium chloride with such scrupulous care that the end-point might be determined with perfect precision and that the precipitate should carry down with it no traces of either of the two factors in the reaction.

Third, a new sample of this same perfectly pure lithium chloride must be converted into perchlorate in such a way that all of the first substance should be converted into the second without loss, and that the lithium perchlorate which results should be perfectly pure and free from contamination with the solids taken from the vessels during the reaction, from moisture, and from dissolved gases.

These conditions may all be fulfilled within a reasonable limit of accuracy. That is, indeed, the reason why lithium perchlorate was chosen; for lithium perchlorate has the properties needed, and none of the other perchlorates seem to possess them.

In the execution of the program, lithium chloride was fused in a bottling apparatus made of fused quartz. At a bright-red heat, hydrochloric acid gas was passed over the fused mass, so that any hydroxide which might have been formed during the

earlier part of the dehydration should be converted back into chloride. The gaseous current was then replaced by pure nitrogen until all traces of acid had disappeared from the gas issuing at the end of the tube, when the pure, limpid, colorless lithium chloride was cooled and weighed wholly out of contact with moisture. By the methods so often described, with but slight modification, the quantities of silver and of silver chloride exactly equivalent to a given weight of lithium chloride were determined. From these results the atomic weight of lithium was found to be 6.939, over 1 per cent lower than the value found by Stas, whose work with this element seems to have been less fortunate than with any other.

Again, similar portions of perfectly pure lithium chloride were treated in flasks of pure fused quartz with a slight excess of perchloric acid. The resulting hydrochloric acid, together with all the moisture, was expelled by air, and the lithium perchlorate after protracted fusion at 300° in dry air was cooled and weighed. The figures may be found in the appropriate part of the full paper; it is enough to say here that since each gram of lithium chloride was found to correspond to 2.54455 grams of silver and to 1.50968 grams of oxygen, the atomic weight of silver is $\frac{2.54455}{1.50968} \times 64.000 = 107.871$. (12.)

Let us turn now to the second general method of determining atomic weights, namely, that which depends upon Avogadro's Rule—a method which is applicable only to gases. Theory states that the weights of like volumes of different gases under similar conditions are proportional to the molecular weights of the substances concerned. If one knows the number of atoms in the molecule in each case, the relative atomic weights are likewise decided. For example, if a given volume of hydrogen weighs 1.008 grams and the same volume of oxygen under similar conditions weighs exactly 16.000 grams, we have a right to conclude from Avogadro's Rule that the molecule of oxygen weighs 15.872 times as much as the molecule of hydrogen. If each molecule of oxygen and each molecule of hydrogen is made up of two atoms, the atomic weights must also be nearly in the

proportion of 16.000 to 1.008. Theoretically, the method is an elegant one. Granting Avogadro's Rule, the chief difficulties which are met are twofold. In the first place it is not easy to measure with very great exactness the weights of such a bulky material as a gas. The globe containing the gases must weigh much more than the gas itself, and is peculiarly subject to the changes of buoyancy of the air. The exact fixation and duplication of temperature and pressure so that the gases may be compared under precisely similar conditions is difficult. Moreover, the perfect purity of the gas to be weighed is not always easily assured. Nevertheless, these difficulties may be in large measure overcome.

A more fundamental difficulty is the fact that Avogadro's Rule holds within the limit of experimental error for actual gases only when they are almost infinitely expanded and therefore have practically no weight in any reasonable volume. Only the perfect gas can be assumed to comply exactly with Avogadro's Rule, and all actual gases are imperfect. Today we know far more about the causes of imperfection than of old; and we are able from the behavior of a gas at several different pressures under measurable conditions to extrapolate to the condition of infinite dilution with some degree of success. Among others, van der Waals, D. Berthelot, Ph. A. Guye, and van Laar have contributed especially toward the solution of the problem (13). Particularly in comparing similar gases such as oxygen and nitrogen the extrapolation, if in error, may be assumed to possess about the same error in each case, and therefore, to cause the approximate elimination of the error in comparison of the two. Nevertheless all extrapolations are uncertain; and there is still a measure of doubt with regard to the extrapolation of the density of any gas to infinite dilution according to any of the accepted methods of accomplishing this result. Accordingly, this method of determining atomic weights, while giving valuable confirmatory evidence, can hardly at present be considered as exact as the classical method of quantitative analysis.

It is a happy circumstance that usually the results of these two widely different methods confirm one another as well as

could reasonably be expected. The mutual confirmation augments our confidence in each.

The third method of determining atomic weights is another purely physical method; it depends, as has been said, upon the varying inertia of atoms of different masses. This method, then, measures mass, rather than weight. It is true that since mass and weight seem always to go hand in hand, the measurement of one is equivalent, for practical purposes, to the measurement of the other; nevertheless the two properties of matter are very different indeed in their nature, and unless we accept the logic and conclusions of Einstein and his followers, we find it hard to formulate any reason for their close parallelism, but must simply accept it as a fact.

The improved method of Aston (6), which utilizes the varying inertia of single atoms, may be briefly described as follows: Molecules and free atoms of a very rarefied gas are highly electrified positively at an anode in an electric vacuum tube. These positively charged atoms and molecules are passed through an arrangement of fine slits so as to form a narrow beam of rapidly moving electrified particles. The beam is deflected by being passed between highly electrified positive and negative plates, the deflection being greater the less the velocity and the less the weight of each particle in question. This fan-shaped beam of rapidly moving particles is then focused by means of a magnetic field, which eliminates in a very ingenious manner the question of velocity and focuses all the particles of any one weight together at one spot. These focused beams of moving particles are registered upon a suitably placed photographic plate, which is affected by the electrified particles in each spot as it would be by light. A given mixture of particles thus produces a number of spots or lines upon the photographic plate, and the mass corresponding to each of these several lines may be measured on a scale determined by the lines similarly produced by substances of known molecular or atomic weight. The method is therefore a comparison of masses in which unknown atomic masses are compared with known ones, these last being fixed by the chemical atomic weights. As far as exactness is con-

cerned this method obviously rests, like the second method, ultimately upon the method of quantitative analysis which determines the relative weights of the substances used as standards. As will be seen later, this third entirely different method of determining atomic weights has yielded remarkable results. When properly interpreted these results confirm in every case our table of the atomic weights of the elementary substances as they exist on the earth's surface.

The correlation of these different methods is an important matter, since no one of them covers the whole ground. The first method depending upon quantitative analysis furnishes the best basis for determining the *equivalent combining weights* of all the elements except those which refuse to enter into chemical combination, such as argon. It fails, however, to give a means of discriminating between the various possible multiples and submultiples of the combining proportions which ought to be chosen to represent the atomic weights.

The second method, depending upon gas density, fixes *molecular* weights, and thus affords just the criterion which was lacking in the analytical method. It is even able, in cases where the gaseous element produces several compounds which may be vaporized, to decide an atomic weight without the assistance of the first method. Nevertheless, the second method is applicable only to those substances which may be vaporized at moderate temperatures.

The third method, that of the mass spectrograph, likewise applies only to gases and vapors. Its great advantage lies in the fact, already stated, that it is capable of sorting, into groups, atoms which differ only in mass. The standard of reference of all these methods at present rests, as already stated, in the results of quantitative analysis.

Adequate discussion of the correlation of the three methods, which has found remarkable justification in the fact that the formulas based upon it correspond admirably to the actual behavior of matter, and in the further fact that the periodic system of the elements based upon it is completely confirmed by the most recent discoveries concerning the atomic numbers

and isotopes, would be too lengthy for further presentation here (14).

Having thus presented very briefly a sketch of the three methods employed for determining atomic weights I shall now touch upon some of the problems, concerning these highly important quantities, which are significant in chemical thought today. These problems are:

First, The question as to the uniformity or constancy of the atomic weights of the elements on earth.

Second, The precision of Faraday's Law.

Third, Evidence from atomic weights as to whether or not the elements are all aggregates of hydrogen.

Fourth, The varying atomic weights of lead, and the discovery of isotopes.

Fifth, The relations of the atomic weights of the factors and products of atomic disintegration.

Sixth, The relations of these phenomena to cosmic theory and other general considerations.

THE CONSTANCY OF ATOMIC WEIGHTS

The question as to the uniformity or constancy of the atomic weight of any given element is an important one. Obviously, if atomic weights are variable the method of attack becomes more complicated than if they are constant, although not less important.

That the atomic weight of any element is essentially the same in different combinations was proved within a moderate degree of accuracy by Stas, who obtained values for silver (15) in different compounds (referred to oxygen) varying between 107.921 and 107.943. In passing one may note that this variation shows about the range of experimental error in his quantitative work, while the difference between his average value 107.93 and the present accepted one (about 107.875) gives the amount of impurity in Stas's silver. Usually, as far as Stas's experiments were able to prove the point, atomic weights of a given sample of material could be taken as constant in different compounds. This conclusion has been amply verified with greater accuracy

since that time. Indeed, upon it rests the method of computation of atomic weights, and because the method yields consistent results within the limit of experimental error, we conclude that the assumption is warranted. The change of mass produced by the loss of an electron or two (if electrons have weight) would be too small to be perceived and the mere transfer of an electron from one atom to another would, of course, have no effect on the weight. That the total weight of reacting substances changes, if at all, less than a millionth of its value during chemical reaction was shown by Landolt seventeen years ago (16).

The evidence afforded by all such experimental results was not adequate to show that every different sample of silver has the same atomic weight. The question as to the uniformity of different samples still remained open, since Stas used silver from only one source, so far as is known.

That different specimens might have different atomic weights is by no means a new idea. Long ago, Cooke seriously considered the question with regard to crystallized compounds of zinc and arsenic, Schützenberger thought that he had detected a variation in the atomic weight of oxygen, Butlerow cited similar cases, and Crookes resurrected the idea as applied to yttrium (17). In time, however, it was shown that variations were either due to experimental error, or to the phenomenon of solid solution which yielded varying proportions under varying circumstances. Apparently none of the earlier investigators sought to find if samples of the given element taken from different parts of the earth possess the same atomic weight. Accordingly in 1886, at the very beginning of my own researches on this subject, the latter question received attention. Copper from Lake Superior was compared as to its atomic weight with copper from Erzgebirge and precisely the same value was found. Later silver, barium, sodium and other elements were compared as to their atomic weights from a geophysical standpoint, and identity within the limit of experimental error was found (18). It appeared then that the atomic weight of each of many of the elements is constant, no matter what the earthly source. Further, at my suggestion Baxter compared the atomic weight of

meteoric iron and later that of meteoric nickel with those of the same elements found upon earth (19). Here again essential identity was proved, showing that this uniformity exists beyond the earth's immediate surface and perhaps includes the whole solar or even the whole cosmic system, since no one knows exactly the source of the Sonora (Mexico) fall whence the specimens came, except that the meteorite certainly came from outside the immediate terrestrial environment.

The sum and substance of these researches showed then that atomic weights are phenomena of extraordinary consistency and therefore possess great significance. Here the subject rested until 1913, when a kind of lead, apparently evolved in uranium minerals in times more recent than that of the solidification of the earth, was found, at Harvard and elsewhere, to have a lower atomic weight than ordinary lead (20). Baxter (21) who had already studied the atomic weight of one or two samples of ordinary lead, gladly extended his research to include samples from all parts of the world and proved that *ordinary* lead is no exception to the rule of uniformity. This new kind of *uranium-lead* then constituted the sole known exception to the rule. It is found (sometimes mixed with ordinary lead) only in uranium minerals. Lead still remains the only certain case of any element, of which any sample, as found on the earth, shows a difference in atomic weight from any other sample of the same element. Irène Curie has published a brief preliminary paper on the possible existence of a similar circumstance with regard to chlorine, but so far as I know this investigation has not reached the final state (22). The exception in the case of lead, now well known to all chemists, thus appeared to be a unique circumstance. It will be discussed later in some of its bearings under the heading "Isotopes."

Atomic weights having thus been shown before the beginning of this century to possess a remarkable degree of constancy, their investigation appeared to be simplified, and the hope of an intelligible outcome of careful study was increased. This being the case, I thought it worth while for a number of years to devote considerable time to the study of these important

Table of atomic weights, 1923

NAME	SYMBOLS	ATOMIC WEIGHTS	NAME	SYMBOLS	ATOMIC WEIGHTS
Aluminium.....	Al	26.96	Manganese.....	Mn	54.93
Antimony.....	Sb	121.77	Mercury.....	Hg	200.61
Argon.....	A	39.91	Molybdenum.....	Mo	96.0
Arsenic.....	As	74.96	Neodymium.....	Nd	144.27
Barium.....	Ba	137.37	Neon.....	Ne	20.2
Bismuth.....	Bi	209.00	Nickel.....	Ni	58.69
Boron.....	B	10.82	Nitrogen.....	N	14.008
Bromine.....	Br	79.916	Osmium.....	Os	190.8
Cadmium.....	Cd	112.41	Oxygen.....	O	16.000
Caesium.....	Cs	132.81	Palladium.....	Pd	106.7
Calcium.....	Ca	40.07	Phosphorus.....	P	31.024
Carbon.....	C	12.000	Platinum.....	Pt	195.23
Cerium.....	Ce	140.25	Potassium.....	K	39.095
Chlorine.....	Cl	35.458	Praseodymium.....	Pr	140.92
Chromium.....	Cr	52.01	Radium.....	Ra	225.95
Cobalt.....	Co	58.97	Radon (Niton).....	Rn	222.0
Columbium.....	Cb}	93.1	Rhodium.....	Rh	102.91
Niobium.....	Nb}		Rubidium.....	Rb	85.44
Copper.....	Cu	63.57	Ruthenium.....	Ru	101.7
Dysprosium.....	Dy	162.52	Samarium.....	Sa	150.43
Erbium.....	Er	167.7	Scandium.....	Sc	45.10
Europium.....	Eu	152.0	Selenium.....	Se	79.2
Fluorine.....	F	19.00	Silicon.....	Si	28.06
Gadolinium.....	Gd	157.26	Silver.....	Ag	107.880
Gallium.....	Ga	69.72	Sodium.....	Na	22.997
Germanium.....	Ge	72.60	Strontium.....	Sr	87.62
Glucinum.....	Gl}	9.02	Sulfur.....	S	32.065
Beryllium.....	Be}		Tantalum.....	Ta	181.5
Gold.....	Au	197.2	Tellurium.....	Te	127.5
Helium.....	He	4.00	Terbium.....	Tb	159.2
Holmium.....	Ho	163.4	Thallium.....	Tl	204.39
Hydrogen.....	H	1.008	Thorium.....	Th	232.15
Indium.....	In	114.8	Thulium.....	Tu	169.4
Iodine.....	I	126.932	Tin.....	Sn	118.70
Iridium.....	Ir	193.1	Titanium.....	Ti	8.0
Iron.....	Fe	55.84	Tungsten.....	W	184.0
Krypton.....	Kr	82.9	Uranium.....	U	238.17
Lanthanum.....	La	138.91	Vanadium.....	V	50.96
Lead (ordinary) }	Pb	207.20	Xenon.....	Xe	130.2
Lead (Uranium) }		206.06	Ytterbium.....	Yb	173.6
Lithium.....	Li	6.939	Yttrium.....	Y	89.0
Lutecium.....	Lu	175.0	Zinc.....	Zn	65.38
Magnesium.....	Mg	24.32	Zirconium.....	Zr	91.0
			Atomic Number 72...	(?)	179.(?)

The usually accepted value for silver (107.880) is adopted in order to avoid confusion. If silver is taken as 107.872 (perhaps the more probable value) instead of 107.880, most of the elements would have their atomic weights lessened by 0.0074 per cent, and nitrogen would possibly have its value reduced to 14.003. Those referred directly to oxygen alone would, of course, be unchanged.

quantities. The outcome of this work (18) which has been generously supported by the Carnegie Institution of Washington and other sources, together with the similar outcome of the work of many other investigators, especially G. P. Baxter, is included in the table below.

This table was prepared by G. P. Baxter and myself for our own use and that of the Sub-Committee on Atomic Weights appointed by the Union Internationale de la Chimie Pure et Appliquée. It is not the international table, but seems to be worth printing now because the old international table of 1921 is out of date, and a new one has been delayed because of the illness of one of the Committee and the time required for international communication. As is customary in stating scientific data, each value includes one uncertain figure: the uncertainty of the last decimal may be only one unit or it may be as much as five units. With the decimal notation closer definition is not possible without a special statement in each case. No pretension is made that the table is ultimate; it merely represents the present opinions of two interested chemists concerning the important quantities with which it deals.

THE PRECISION OF FARADAY'S LAW

Closely connected with the gravimetric relations of atomic weights as they are found from the combining proportions is the relation of the weights of the same substances precipitated from their solutions by a given quantity of electricity. After the fundamental law showing that the chemical equivalents are proportional to the electrochemical equivalents was discovered by Faraday (23) in 1834, and shown by him to be at least approximately true, Lord Rayleigh and Mrs. Henry Sidgwick, as well as Kohlrausch and others, had narrowed the possible range of error by painstaking and accurate investigations (24). At the time of the investigation upon the atomic weight of copper already mentioned, it appeared, however, that the then accepted value of the electro-chemical equivalent of copper was distinctly less than the new and unquestionably accurate chemical equivalent of that element. Therefore it seemed worth while

to investigate this subject anew; and I spent considerable time with the help of two able assistants in discovering where the cause of the discrepancy might lie. It was found to lie not in any fault in the exactness of Faraday's Law, but rather in a side-reaction which caused some of the deposited copper to dissolve during the act of electrical deposition. By the choice of suitable conditions correction could be applied for this disturbing circumstance, and Faraday's Law was proved to hold with exactness, within the limit of error of carefully performed and very precise experiments. Moreover, silver was found to possess precisely the same electrochemical equivalent when deposited from a solution of silver nitrate in fused potassium and sodium nitrates at 250°, as from aqueous solutions at room temperature (25). There can be no question, then, that Faraday's Law ranks among the most precise of the laws of Nature. This conclusion reënforces one's belief in the significance and importance of the atomic weights.

The electrochemical equivalents have rendered yet another service in this connection. Millikan (26) having determined with great exactness the value of the unit electric charge (the electron), we have, through the electrochemical quantity associated with the atomic weight in grams, a simple method of discovering the number of atoms in this weight, and therefore the actual weight of a single atom. The number of atoms in 63.57 grams of copper, or 16.00 grams of oxygen, or 107.88 grams of silver, for example, is shown thus in each case to be over six hundred sextillions (0.6062×10^{24}).

ARE THE ELEMENTS ALL CONDENSATIONS OF HYDROGEN?

In the search for the underlying laws regulating the phenomena of Nature, man seeks always to simplify his assumptions as much as possible. Generally, this is an advisable procedure, although sometimes he carries the simplification too far. Concerning the definite quantities now under consideration an obvious simplification arose very soon in the history of the subject. Prout's suggestion (2) that all elements might be simply multiples of hydrogen followed only twelve years after

the idea of atomic weights had been propounded by John Dalton (1) in 1803. Oxygen, for example, might be simply an aggregate of ten hydrogens bound together by a superchemical affinity, which ordinary agencies could not overcome, since the atomic weight of oxygen was supposed by Prout to be ten times that of hydrogen. It is true that this notion of Prout's arose partly from the fact that in those days it was customary to drop all the decimal places in the atomic weights; hence these values appeared to be whole numbers, when they were really incommensurable. The instance is an interesting case of a suggestive generalization based upon false premises.

Prout's hypothesis has had a very varied career. Stas thought that he had completely demolished it when he found for potassium the value 39.14, and for chlorine 35.45, with possible errors not greater than 0.1 per cent (15). It appeared to be certain that if a single primordial element existed, it must be at least as small as one-tenth or perhaps one-twentieth of the gravimetric magnitude of hydrogen. As the precision of determinations increased, the apparent incommensurability of atomic weights increased. Such numbers as 107.88, 39.10, 63.57, 126.932, 79.916, to mention the most accurate modern determinations of certain well known atomic weights, defied the discovery of any simple proportionality. Nevertheless, a haunting affection for Prout's hypothesis still persisted among a few investigators, sometimes together with an unwarranted distrust in the carefully determined values. Even some of those who wisely pinned their faith upon established fact were supported in their lingering belief in Prout's hypothesis by the undoubted circumstance that some, at least, of the atomic weights (far more than mere chance would allow) showed a striking tendency to approach whole numbers. This was suggested by Mallet long ago, and pointed out convincingly by R. J. Strutt, now Lord Rayleigh (27). Notably (to quote the most recent values) carbon 12.000, nitrogen 14.008, oxygen 16.000, fluorine 19.00, phosphorus, 31.024, sulphur, 32.06, and arsenic 74.96, besides a number of others, showed a very close approach to commensurability with the sixteenth part of the oxygen atom, which frac-

tion is not far from the atomic weight of hydrogen. The deviations of the large majority of the elements from whole numbers nevertheless remained. The situation presented an interesting example of a rule which held only for a minority of cases, and yet a rule which could not be wholly discarded, because it appeared to be justified in a larger number of cases than the doctrine of chance could justify. The solution of this problem and the vindication of Prout's hypothesis as a reasonable, although not fully proved generalization, is soon to be discussed.

Prout's hypothesis was the beginning of a host of endeavors to find relations between the atomic weights. The names of Pettenkofer, Lennsen, Cooke and Gladstone among many others are associated with the growing generalization. As is well known, these endeavors first dealt with several groups or families of similar elements, such as chlorine, bromine and iodine. Later, attempts were made to relate the groups to each other, but it was not until rational criteria for deciding upon atomic weights were confirmed by Cannizzaro in 1858 that the relation of the atomic weights to the properties of matter was made clearly manifest by de Chancourtois, Newlands, Mendeléeff and Lothar Meyer in the sixties of the last century (28).

The brilliant discovery of the periodic classification of the elements laid a basis for the study of inorganic chemistry which has afforded and will in the future afford priceless help in the development of this subject. Space is lacking here for further presentation of this important aspect of atomic weights, but the ingenious contribution of Rydberg should be noted (28). We must turn to more recent advances in knowledge.

THE DISCOVERY OF ISOTOPES

Within the last twenty years the unique discoveries (29) of Becquerel, Marie and Pierre Curie, Rutherford, Soddy, Ramsay, Boltwood and others have brought to the century-old hypothesis of Prout, a support hitherto undreamed, and have shown at the same time that the alchemists "builded better than they knew." The story is well known. Becquerel, seeking to discover whether or not uranium could transform sunlight

into X-rays, found to his amazement that this element is continually emitting enigmatical rays of several kinds even without the assistance of sunlight. At his suggestion Madame Curie sought to discover if any other substances possessing similar radioactivity might exist; and thus she discovered, at first working alone, and later with the help of her husband, the new and extraordinary element radium.

The investigations of Rutherford, Soddy and Ramsay, and others (29) showed beyond reasonable doubt that radium is spontaneously disintegrating at a definite rate not to be accelerated or retarded by any artificial means, yielding helium together with a transient emanation. This emanation, called by Ramsay, "niton," and very recently renamed "radon," is believed to be the highest number of the argon series, possessing an atomic weight of about 222. Like other elements in its vicinity in the periodic system, it is highly unstable and breaks down by a succession of steps. Our best evidence points with great probability to lead (30) and helium as the final end-products of this disintegration. Moreover, since radium is usually found in minerals in quantities approximately proportional to their uranium contents, it is generally believed that radium itself is a disintegration product of uranium—the radioactivity of uranium and its components being due to the several processes of disintegration (some of them exceedingly slow) which occur in these substances. The resulting helium would, of course, remain imprisoned in the mineral. Thus was explained the anomalous existence of an inert gas in uranium minerals, which gas had been discovered by Hillebrand in 1890 and shown to be helium by Ramsay (and also by Clève) in 1895 (31).

As regards the present topic, the discovery of atomic disintegration presents many points of very great interest. Obviously if uranium disintegrates by successive steps into nothing but helium and lead, with radium as an intermediary transient product, the atomic weights of these four elements, uranium, radium, lead, and helium should show definite additive relations. According to a highly interesting hypothesis which has been supported in many ways and which has gradually grown

by the accretion of the ingenious contributions of Russell, Fleck, Soddy, and Fajans (29), such a simple additive relation indicates that lead, if formed in this way, should possess the low atomic weight of about 206, instead of the value 207.2 possessed by ordinary lead. As Sir William Ramsay pointed out to me in 1912, the question as to the atomic weights of these several elements became therefore a crucial question as regards the whole theory of radioactivity. The accurate determination of the atomic weight of uranium-lead could alone furnish results which would conclusively prove or disprove the point. If this lead possessed the atomic weight 206, the evidence for the new theory would be very strong. The question was of profound import as regards the composition of the elements, for light upon these four elements must furnish priceless information concerning the nature of elements in general.

With the foregoing conclusions in mind, Fajans sent one of his assistants, Max Lambert, to the Wolcott Gibbs Memorial Laboratory in order that he might determine the atomic weight of a specimen of radioactive lead obtained from the uranium mines of Joachimsthal, Bohemia. Careful research (20) proved that this lead had an atomic weight, although not quite so low as 206, nevertheless so much below 207 as to support at least qualitatively the Soddy-Fajans theory of atomic disintegration (29). This was the first case in which any real discrepancy had been found between the atomic weights of different specimens of the same element. The two kinds of lead were found to be practically identical in every respect, except those which concern weight. Specimens of an elementary substance thus apparently identical in every respect except in their gravimetric relations have been named *isotopes* by Soddy. Nearly simultaneously and quite independently the conclusion was further supported by similar results obtained by Maurice Curie (32) in Paris and Otto Hönigschmid (33) in Vienna. The metal at first investigated by all the experimenters was not pure uranium lead, being mixed with ordinary lead in the crude mineral. Hence it was not surprising that the results were not quite as low as 206. Accordingly it became a matter of great importance as

regards the theory to obtain lead from selected pure crystals of the two uranium minerals, bröggerite and cleveite, in order to avoid any admixture of common lead from another source.

Dr. Ellen Gleditsch of Christiania very kindly provided me with a small specimen of pure uranium lead, obtained by careful selection of pure crystals of uranium mineral; these were analyzed in the Wolcott Gibbs laboratory (34). About the same time Otto Hönigschmid (35) obtained similar specimens from Norway and from Africa. The two results for the atomic weight were respectively 206.08 and 206.05, proving beyond a shadow of doubt that pure uranium-lead really has an atomic weight of very nearly 206, as demanded by the theory.

The atomic weight of uranium, the starting point of the disintegration theory, then assumed extreme importance. This atomic weight had always been a matter of interest, since it is the greatest among all the elements. Even before the birth of knowledge of radioactivity I had begun to investigate it, and had proved, while this knowledge was still in its infancy, that the formerly accepted value 240 was much too high (36). There could be no question that the true value must be at least as low as 238.5. Twenty years later, using the method which had been elaborated in obtaining this last mentioned result, together with the approved appliances and the fused quartz apparatus, which had become available in the intervening years, Hönigschmid found the value 238.18, which stands today as the most likely value for this atomic weight (37). He determined also radium as 225.96, having previously come to Cambridge for the purpose of learning the necessary technique. Since the atomic weight of helium had been proved by the method of gas density to be not far from 4.00, all the data were now at hand with which to test the simple additive calculation; upon this calculation the theory of radioactivity must stand, or fall.

Uranium is supposed to yield one atom of radium and three atoms of helium during the earlier stages of the disintegration. The difference between the atomic weights of the two metals should then be 12.0. It appears as a matter of fact to be 12.18. In other words, if radium is 226, uranium should be 238, or if

uranium is really 238.2, radium should be 226.2. The discrepancy is not great, but it is perhaps beyond the error of experiment.

Let us turn to the later stages of the disintegration. Radium is believed, after five emissions of helium, finally to reach the stage of lead. This should mean a difference in the atomic weights of 20.0 if helium is 4.0. Therefore if radium is 225.96, the lead produced by its disintegration should be 205.96. The mean between the values for lead calculated from uranium on the one hand, and radium on the other, is 206.07. As already stated, the atomic weight of pure uranium lead was found to be 206.06. The differences are indeed very small.

The element thorium seems to be disintegrating in a similar way, yielding a form of lead having the atomic weight 208; but its case has not been so thoroughly investigated. Ordinary lead may be a mixture of these two kinds, or may contain yet a third variety.

On the whole, then, the theory of atomic disintegration seems to be well supported by the several atomic weights, and receives from them a justification far greater than it could attain without their aid.

The simple additive relation just discussed, involving nearly whole numbers, leads one to consider the deviations from whole numbers shown by many other atomic weights, such as those of chlorine, copper and zinc, as well as a number of other common elements. The discovery, just discussed, that a given element might be composed of two isotopes having two atomic weights and yet possessing in these separate samples all other properties essentially similar, threw a flood of light upon the previously incomprehensible anomaly presented by the irregular numbers. Since lead thus possesses isotopic variation, may not other elements also possess the same kind of variation; and may not such a value as that for chlorine 35.46 be ascribed simply to the assumption that chlorine is a mixture of about one part of atoms having a weight 37, with three parts of atoms having a weight 35? Such different specimens of chlorine, possessing essentially identical properties, could not be separated by any

ordinary chemical or physical means. Therefore they must persist together in constant proportion, if they had once been thoroughly mixed.

This possibility had indeed been suggested by J. J. Thomson (5) in 1912, before the first positive discovery of the isotopes of lead, in another case, namely, that of the rare gas neon. By his method depending upon the electrical deflection of positive rays in an atmosphere of neon, Thomson had concluded that this gas was composed of two atoms of two different kinds, most of the atoms having the atomic weight of 20 and some of them having the atomic weight 22. The mixture possessed the already ascertained atomic weight (as found by the gas-density method) of 20.2. Thomson's method had not been perfected to a high degree of refinement, and the curved images upon which the conclusions were based formed a hardly convincing argument in favor of the contention. Subsequently the method was greatly improved by F. W. Aston in the famous Cavendish laboratory and developed into the "positive ray spectrograph" or "mass spectrograph," which has already been described as the third method of determining atomic weights (6). By this means Aston has shown with a high degree of probability, that as a matter of fact many elements appear to consist of mixtures of two or more isotopes, each isotope having an atomic weight which is nearly a whole number. A somewhat different, but equally interesting and important method of attaining the same result has been devised by Dempster (6), whose results agree, as a rule, with Aston's. The interpretation of the photographic slides recording the results is not, to be sure, always easy. Nevertheless any one who has carefully studied the evidence can hardly fail to agree with the conclusion. The values of the atomic weights of the several isotopes taken from Aston's most recent reports are given in the following table.

The first column of the table contains the names of the elements and the second column the symbols, as in the table of atomic weights, but arranged in the order of the atomic numbers.

The third column contains the atomic number, a quantity not yet mentioned. This atomic number is simply the serial

Table of isotopes

ELEMENT		ATOMIC NUMBER	ATOMIC WEIGHT	MINIMUM NUMBER OF ISOTOPES	ATOMIC WEIGHTS IN ORDER OF IMPORTANCE
Name	Symbol				
Hydrogen.....	H	1	1.008	1	1.008
Helium.....	He	2	4.00	1	4.00
Lithium.....	Li	3	6.939	2	7; 6
Glucinum.....	Gl	4	9.02	1	9
Boron.....	B	5	10.82	2	11; 10
Carbon.....	C	6	12.000	1	12
Nitrogen.....	N	7	14.008	1	14
Oxygen.....	O	8	16.000	1	16
Fluorine.....	F	9	19.00	1	19
Neon.....	Ne	10	20.2	2	20; 22
Sodium.....	Na	11	22.997	1	23
Magnesium.....	Mg	12	24.32	3	24; 25; 26
Aluminium.....	Al	13	26.96	1	27
Silicon.....	Si	14	28.06	2	28; 29; (30)
Phosphorus.....	P	15	31.024	1	31
Sulfur.....	S	16	32.065	1	32
Chlorine.....	Cl	17	35.458	2	35; 37
Argon.....	A	18	39.91	2	40; 36
Potassium.....	K	19	39.095	2	39; 41
Calcium.....	Ca	20	40.07	(2)	40; (44)
Iron.....	Fe	26	55.84	(1)	56; (54?)
Nickel.....	Ni	28	58.69	2	58; 60
Zinc.....	Zn	30	65.38	4	64; 66; 68; 70
Arsenic.....	As	33	74.96	1	75
Selenium.....	Se	34	79.2	6	80; 78; 76; 82; 77; 74
Bromine.....	Br	35	79.916	2	79; 81
Krypton.....	Kr	36	82.9	6	84; 86; 82; 83; 80; 78
Rubidium.....	Rb	37	85.44	2	85; 87
Tin.....	Sn	50	118.70	7(8)	120; 118; 116; 124; 119; 117; 122; (121)
Antimony.....	Sb	51	121.77	2	121; 123
Iodine.....	I	53	126.932	1	127
Xenon.....	Xe	54	130.2	9	129; 132; 131; 134; 136; 128; 130; 126; 124
Caesium.....	Cs	55	132.81	1	133
Mercury.....	Hg	80	200.6	(6)	(197-200); 202; 204

number of each element in the order of the periodic system—hydrogen occurring first in the series, receives the number 1, helium, the second element, 2, and so on. This order is usually the order of the atomic weights, but there are a few cases, to

be mentioned later, in which the two orders are different. The idea of giving numbers as well as atomic weights to the elements was probably first proposed by Newlands, one of the founders of the periodic system of the elements; it appears in one of the earliest of his papers (38). Newlands had no other basis for the assignment of these numbers than the order of the atomic weights, and since many of the elements were unknown at that time, his atomic numbers differ greatly from ours, especially toward the latter part of the system; but the idea of possible significance in the atomic numbers should be ascribed to him. No other basis than the positions of the atomic weights in the periodic system was indeed available for the assignment of atomic numbers (which appeared in Newlands's time to be rather arbitrary and transitory) until the brilliant discovery of Moseley (39) that the X-ray spectra of the elements show definite harmonic progression. This progression is found to coincide more reasonably with the properties of the elements in the periodic system than the order of the atomic weights. The more reasonable ranking legitimized by the new atomic numbers is particularly obvious in the case of nickel and cobalt, and also in those of tellurium and iodine, and of potassium and argon. In each of these cases the order of the atomic weights transposes the elements out of their true positions, whereas the order of the atomic numbers of Moseley ranks these elements satisfactorily. We must not forget, however, that the original discovery of the periodic system was due entirely to the study of atomic weights, and that even the anomalies above named had been correctly appraised, although not explained, long ago.

The fourth column of the above table needs no further explanation, since it merely repeats the chemical atomic weights given in the previous table; but the fifth column records a new series of facts—the minimum number of isotopes in each case. It will be seen that 15 of the elements apparently have only one isotope apiece. These are among the elements which had been known for a long time to give nearly whole numbers for their atomic weights.

The sixth column exhibits, in simple whole numbers, the atomic weights of the several isotopes as found by the "mass spectrograph." The values are considered as accurate to within perhaps 0.1 per cent. With elements consisting of only one isotope, the single value is, of course, the same as the atomic weight within the limit of error; on the other hand, with those elements consisting of two or more isotopes, the chemical atomic weight lies somewhere between the extreme values for the several isotopes, depending upon the proportion of the mixture. When only two isotopes are present, the proportions of mixture can be easily determined from the atomic weight of the mixture—that is to say, the chemical atomic weight (column 4). Examples may clarify this explanation. Thus under boron (B) the fifth element in the table, the numbers 11 and 10 are given in column 5, meaning that boron has two isotopes, one (the more plentiful) having the atomic weight 11.0, and the other (less plentiful) having the atomic weight 10.00. These are mixed in such proportion that the resulting mixture has the chemical atomic weight of 10.82 (column 4). Chlorine (Cl) is seen to consist of two isotopes, having the atomic weights 35 and 37 (column 6), which must be mixed in the proportions indicated by the net value 35.458.

As already stated, the processes of Nature are not usually, if ever, capable of separating isotopes which have once been mixed. Here as in so many other chemical exigencies, man can accomplish artificially, by taking thought, ends which are beyond the reach of natural agencies. To effect physical separation, one must take advantage of differences of physical or chemical behavior; and the only respect in which isotopes of a given element behave differently from one another is with regard to those properties which depend upon weight or mass. The attempt to separate the isotopes in specimens of the elements possessing two or more of these varieties has already been crowned with partial success. Brönsted and Hevesy (40) were the first to obtain, by fractional distillation under highly diminished pressure, specimens of mercury having slightly different specific gravity. The determination of density is in such cases a means

of determining atomic weight, for it had already been shown that the atomic volumes of two isotopes of lead (and therefore presumably the atomic volumes of other isotopes) are identical (34).

Harkins and Mulliken (41) have repeated this work even more successfully, and effected also a partial separation of chlorine; and others have obtained similar evidence with regard to other elements. Yet other investigations of this kind are in progress, at Cornell, Harvard and elsewhere. As yet, no weighable quantity of isotope (of any elements possessing more than one) has been obtained in a pure state, except in the case of lead, in which the spontaneous disintegration of pure uranium minerals has segregated the single kind of lead at its birth and prevented contamination with common metal.

Thus the existence of fractional numbers among the atomic weights is wholly explained, and Prout's guess (which postulated that the true atomic weights of individual atoms are really whole numbers) is given an extraordinary confirmation of which he never could have dreamed. Even the case of uranium, mentioned before, may be explained upon this basis. Ordinary uranium might possibly consist of two isotopes possessing, let us say, atomic weights of 238 and 242, each yielding the same kind of radium and lead on disintegration, but the heavier atom of uranium yielding one atom more of helium (and two more electrons from its nucleus) than the lighter. Of course an admixture of a large proportion of U_{238} with a small proportion of U_{242} might have the atomic weight 238.2, whereas the lead resulting from each mixture would have the same atomic weight 206. This detailed explanation is hypothetical, but will serve to explain the argument.

The agreement of the results of the mass spectrograph, as thus interpreted, with the present table of atomic weights, as determined by quantitative analysis, is highly satisfactory. For example, whereas Stas gave lithium the value 7.03, more recent investigation (12) has proved that lithium is really 6.94. Aston has shown that without doubt lithium consists of two isotopes having the atomic weights 7.00 (in great preponderance) and 6.00 (in small amount). The consistency of this outcome

with the new value (6.94) and the inconsistency with Stas's less accurate value (7.03) is obvious. Similarly the formerly accepted atomic weight for glucinum (otherwise known as beryllium) was 9.1, which would seem to indicate two isotopes. Recently Hönigschmid has shown that the true value is 9.02, which is consistent with the existence of only one isotope as found by the mass spectrograph. Aston pointed out that a formerly accepted value for silicon, 28.3, was too high to correspond to the very small amount of the higher isotopes present, the chief isotope having the atomic weight 28.00. While this statement was in press, Baxter found 28.06 as much more nearly the true value. In the same way, the older value for boron 10.9 agrees much less satisfactorily with Aston's results than the new value 10.82, found independently by Baxter and Hönigschmid (42).

Less easily explained deviations from the simple whole number rule occur in the cases of hydrogen, at the very beginning of the series (which deviates by 0.8 per cent) and caesium, the next to the last in the table (which deviates by 0.15 per cent). Tin, as indicated by more recent investigations of Aston, is probably to be added to the list of anomalous exceptions (43).

The most interesting of these is hydrogen, not only because its percentage deviation is greatest, but also because of the unique position of hydrogen at the beginning of the ordered tables of both atomic weights and atomic numbers. As guessed by Prout long ago, and Harkins and Aston and many others more recently, hydrogen may be the "protyle" (as Crookes (44) named it) or original substance from which all the other atoms are built. Supposing this to be the case, since hydrogen has only one isotope and an atomic weight of 1.008 (concerning which there can be no doubt) helium should be 4.032, if an atom of helium consists of four hydrogen atoms. Such a deviation from the true atomic weight of helium, 4.00, is far beyond the limit of experimental error. With higher atomic weights the discrepancy would be still greater; with sodium, for instance, which is really almost exactly 23.00 (22.997), the atomic weight should be 23.18, if an atom of sodium consists of an aggregation

of 23 atoms of hydrogen. What is the reason of the many discrepancies of this kind? Do the facts disprove definitively the hypothesis of Prout, simply because of the figure in the third decimal place of the hydrogen value?

Many think today that the hypothesis is not thereby disproved. They prefer to believe that the mass lost by hydrogen when it is converted into helium or any other element, is converted directly into energy, since the theory of relativity points out that the energy and mass of a body vary proportionately to one another, the factor of proportionality being the square of the velocity of light. The argument is an interesting development of modern theoretical physics which time will clarify. For the present we must remember that, after all, no evidence has been obtained on earth that hydrogen can actually be condensed into helium (45). Although such a condensation should yield an enormous outcome of energy and therefore presumably ought to take place easily—judging from the analogy of chemical change which, as a rule (although not always) occurs more easily the greater the change of energy involved, the condensation has not yet been effected experimentally. Perhaps very great pressure and very high temperature together might make possible the condensation of hydrogen into helium. If this is true, the existence of hydrogen is an exaggerated case of “false equilibrium.” Dissociation of helium into hydrogen would hardly be expected, except at very high temperatures in the absence of pressure, or under great electric stress, since it would require the fixation of an equal amount of energy. Although the very heavy atoms such as those of uranium, thorium and radium disintegrate spontaneously (perhaps because their atomic structures are too complex to be stable), all the common elements possess atoms of very great stability and permanence. It is true that Rutherford has obtained strong evidence that under the shock of collision, electrically charged helium atoms, emitted with great velocity from radium, are capable of causing the disintegration of atoms of nitrogen and other elements; but the conditions involved are extreme and highly abnormal (46).

ATOMIC WEIGHTS AND COSMOGONIC THEORY

The outcome of these investigations on atomic weights has a far wider bearing than might appear at first on the surface. Since they concern the ultimate atoms which build up the universe, their significance extends over the whole field of cosmogony in all its ramifications.

In the first place, a word should be said about the bearing of the new discoveries on our guesses concerning the intimate internal structure of the atoms themselves. There is fairly general agreement on the hypothesis that nearly all of the mass of an atom is concentrated in an inconceivably small nucleus in the center, surrounded by electrons (unit charges of electricity) whose number is identical with the atomic number. The possible arrangement of the surrounding electrons has been the subject of many brilliant hypotheses initiated by J. J. Thomson and Rutherford. Bohr has favored orbital systems (47), while Gilbert N. Lewis and Irving Langmuir favor a more definitely fixed arrangement (48). The ideas involve many assumptions; neither seems to suggest a stability of structure corresponding with the amazing indestructibility of most atoms. Therefore the details of these interesting and suggestive considerations do not seem at present to throw much new light upon the questions at issue in the present paper. That the relations of atomic weights and numbers to the harmonic systems of spectrum-lines are necessarily involved in all such hypotheses Cornu, Deslandres, Grünwald and others felt long ago (49). Bohr has translated these ideas brilliantly into the language of electrons and quanta; but the method is not, even yet, free from assumptions. Doubtless as he perceived the harmonic relations of spectrum analysis will be of very great value in assisting us to decide upon a definitive explanation of the internal structure of atoms; and in explaining their cosmic as well as their earthly behavior. The possible arrangement of the "protons" (hydrogen nuclei) in the nucleus of a heavy atom, together with that of the electrons which are supposed to be enchained in the complex heavier nucleus, offers a yet more perplexing puzzle. Lack of space prohibits further discussion on this subject here.

Considering cosmogonic theory as applied to the structure and origin of the earth, we find that the theory of isotopes and the atomic weights of the products of atomic disintegration in the case of uranium and radium give us information otherwise unattainable. Since all the lead on earth (except that found in uranium and thorium minerals) has the same atomic weight, and since other elements also found to possess several isotopes are, so far as is known, made up of the same proportions of these isotopes in each case, whether the elements are found on the established surface of the earth or in meteorites, it is apparent that the mixing of the isotopes must have been accomplished in a very complete fashion before the earth became a single solid entity. Two cosmogonic alternatives are possible as interpretations. The mixing may have resulted in the act of forming the elements in question: in that case the proportions in which the isotopes exist in any earthly elementary substance are significant of the unknown laws which determined the genesis of the elements. On the other hand, the different isotopes may have been produced at different times and in different initial conditions and have been mixed together after their production. When once mixed ordinary cosmic processes would not be likely to separate them. If this latter is the alternative to be chosen, we have in the new fact strong evidence that the solar system was once all in a mobile condition (either liquid or gaseous); otherwise the mixture could not have been completely accomplished.

The latter conclusion seems to militate more or less against the planetesimal theory of the genesis of the earth. The objection to the planetesimal theory becomes still stronger when we consider the case of lead, for in this case we know that the most probable isotopes of lead are uranium-lead with an atomic weight of 206 and thorium-lead with a greater atomic weight of perhaps 208. These two varieties of lead are produced at different rates from different initial substances, and both apparently have been produced separately on the earth since it was solidified, in uranium and thorium minerals respectively. The fact, however, that the great bulk of the lead on earth has

an atomic weight of 207.2 (which may be due simply to a mixture of three parts of thorium lead to two of uranium lead) would seem to indicate that the great bulk of the lead was formed on earth, or at any rate in the solar system, before the separation of the earth, when the matter of which the earth is composed was so mobile as to allow of perfect mixing.

The existence of uranium lead with a low atomic weight in uranium minerals has yet another bearing on cosmogony. The rate of each of the several steps of disintegration of uranium into the end-products helium and lead has been fairly well defined. The complete process requires millions of years to produce any important percentage of lead. Evidently, as has been suggested by Boltwood (30) the percentage of lead in any given uranium mineral ought to give a definite index of the age of this mineral, and therefore an estimate of the minimum time which has elapsed since the mineral appeared in its crystalline form. This criterion as to the age of the earth gives it a very much longer life than had been credited it by the earlier calculations of Kelvin and others. One must, however, be cautious in accepting such estimates without reserve. Uranium minerals are often mixed with ordinary lead from other sources. Merely determining the quantity of lead present may therefore yield too long a period. The verdict from the percentage of lead in uranium minerals is accurate only when the atomic weight of the lead existing in the mineral is known (50). If the atomic weight proves to be exactly 206, showing that the metal in question originated wholly from the uranium mineral, the accuracy of the conclusion is limited only by the accuracy of the calculations as to the length of time required for the disintegration. If the atomic weight is higher than 206, evidently either thorium lead or ordinary lead must be mixed with uranium material, and therefore the estimate becomes uncertain. Thus the determination of atomic weights affords means of validating estimates of time of the order of millions of years, and becomes of great importance in deciding the significance of one of the most promising of our present means of determining the age of the earth.

Turning now from the surface of this planet to the conditions in the sun and stars, we find that the new knowledge concerning the relations of the atomic weights and the phenomena of radioactive disintegration involve important modifications of cosmic theory. That the extreme conditions of temperature and pressure which must obtain in stars might cause disintegration of the heavier elements, or consolidation of the lighter elements into heavier ones, has long been deemed possible (51). The sudden flaring up of inconceivably great hydrogen flames in new stars such as Nova Aquilae not long ago, or the phenomenal new star of Tycho Brahe in 1572, suggests that the evolution of heat in a head-on collision of two heavenly bodies has been enough to disintegrate many of the heavier elements into hydrogen. From whence otherwise could the vast output of hydrogen come? The solar prominences may be produced by a similar process. This view finds support in the resurrection of Prout's hypothesis accomplished by the modern theory of isotopes and the "whole number rule," already explained. It seems to us much more possible today that the elements are really aggregations of hydrogen than it did of old. Rutherford's experiments (46) seem to show, as already stated, that the very violent collision of single atoms may accomplish the disintegration of nitrogen and other elements, with hydrogen as one of the products. Perhaps hydrogen is thus emitted on a gigantic scale during the formation of new stars and of flaming variables.

That the slow disintegration of uranium and radium must be taking place in stellar bodies, if any uranium or radium exists in them, is evident; since this disintegration is, so far as we know, unaffected by temperature. The process involves the output of vast amounts of energy, and gives a much needed theoretical explanation for some of the outpouring of energy from the sun and stars, which is far too great to be accounted for by mere condensation of these bodies. Probably even the additional heat suggested by this explanation is not sufficient fully to account for all that which is actually disengaged, but at least the radioactive theory is a help in this direction.

One is prompted to ask: How could uranium ever have been produced in the first place, since it contains so much potential energy? The case of uranium is exactly opposite to that of hydrogen and helium. Hypothesis tells us that four atoms of hydrogen might combine to form helium with great output of energy, but lead and helium could combine to form uranium only with the intake of all the energy which we find to be given out when uranium spontaneously disintegrates. Since we know of no means of even retarding this disintegration, the possibility of reversing the process experimentally seems very far away. Conditions suitable for synthesizing uranium must be catastrophic in the extreme.

That any of the stable elements should disintegrate with the evolution of energy is improbable; the only way in which energy might be obtained from them would be by forcing them into an atomic merger—a hitherto unattainable outcome.

These speculations are in advance of our knowledge of fact; they are but suggestions as to possible fields of research, many of which lead us far afield from the subject of atomic weights. Nevertheless this subject bears so close a relation to the fundamental processes which must have determined cosmic development that the consideration of atomic weights can never be omitted in any searching investigation of the nature and evolution of the universe.

REFERENCES

- (1) ROSCOE, H. E., AND HARDEN, A.: "A New View of the Origin of Dalton's Atomic Theory," London, 1896.
- (2) PROUT, W.: *Ann. Phil.* (Thomson), **11**, 321 (1815); **12**, 111 (1816).
- (3) AMEDEO AVOGADRO DI QUAREGNA: *J. Phys. Chim. Hist. Nat. et des Arts Paris*, **73**, 58 (1811).
- (4) RICHARDS, T. W.: *Science (N. S.)*, **26**, 303 (1907).
- (5) THOMSON, J. J.: *Proc. Roy. Inst.*, **20**, 593 (1913).
- (6) ASTON, F. W.: *Phil. Mag.*, (6) **38**, 707 (1919); **39**, 611 (1920); "Isotopes" London, 1922. This book should be consulted for many details, both of history and experiment, which can not be treated in the present brief paper. Also, Dempster, A. J., *Phys. Rev.*, **20**, 631 (1922) etc.
- (7) CLARKE, F. W.: *Memoirs of the Nat. Acad. Sci.*, **16**, No. 3. "The Constants of Nature. Part V. A Recalculation of the Atomic Weights," 4th ed., 1920.

- (8) TYNDALL, J.: "Sound," 1st. ed., p. 26, (1867); See also Jevons, "Principles of Science" I. 380, ed. of 1874.
- (9) RICHARDS, T. W.: *Carnegie Inst. Wash. Pub.*, No. 125, 72 (1910).
- (10) RICHARDS, T. W., AND PARKER, H. G.: *Proc. Am. Acad. Arts Sci.*, **31**, 67 (1895); Baxter, G. P., Moore, C. J., and Boylston, A. C., *J. Am. Chem. Soc.*, **34**, 259 (1912); Richards, T. W., and Krepelka, H., *Ibid.*, **42**, 2226 (1920).
- (11) RICHARDS, T. W.: *Proc. Am. Acad. Arts Sci.*, **30**, 385 (1894); Richards, T. W., and Wells, R. C., *Am. Chem. J.*, **31**, 235 (1904); Richards, T. W., *Ibid.*, **35**, 510 (1906).
- (12) RICHARDS, T. W., AND WILLARD, H. H.: *Carnegie Inst. Wash. Pub. No. 125*, 1-48; Summary 87-88 (1910).
- (13) JONES, G.: *J. Am. Chem. Soc.*, **32**, 513 (1910). Phillippe A. Guye and his pupils have published many papers on this method in *J. chim. phys.*, 1906-1922.
- (14) Any adequate textbook on physical or theoretical chemistry explains the criteria for deciding atomic weights. See, for example, "Chemical Principles" by Arthur A. Noyes and Miles S. Sherrill (N. Y. 1922) p. 7, 12 and 91. Even most schoolbooks on chemistry now explain the application of Avogadro's Rule; for example, an especially clear elucidation is given in "Practical Chemistry" by N. Henry Black and James Bryant Conant, p. 128, *et. seq.* (N. Y. 1920). See also "The Standard of Atomic Weights" by Theodore W. Richards, *Proc. Am. Acad. Arts Sci.*, **37**, 179 (1901); *Z. anorg. Chem.*, **28**, 358 (1901).
- (15) STAS, J. S.: "Untersuchungen," (trans. Aronstein 1867), p. 219; Clarke, F. W., *Smithsonian Misc. Coll.*, **27**, No. 2. "The Constants of Nature. Part V. A Recalculation of the Atomic Weights," 1st. ed., p. 261, 1882.
- (16) LANDOLT, H. H.: *Sitzungsb. d. K. pr. Akad. Wiss.*, **16**, 354 (1908).
- (17) COOKE, J. P.: *Memoirs Am. Acad. Arts and Sci.*, (N.S.), **5**, 23 (1854); Schützenberger, P., *Chem. News* **45**, 50 (1882); Crookes, W., *Nature*, **34**, 423 (1886); Butlerow, A., *Ber.*, **15**, 1559 (1882).
- (18) For a summary of this work and bibliography of the earlier contributions, consult *Carnegie Inst. Wash. Pub. No. 125*, 53, 91 (1910). All my more recent papers on this subject have appeared in the *Journal of the American Chemical Society* and can easily be found there.
- (19) BAXTER, G. P., THORVALDSON, T.: *J. Am. Chem. Soc.*, **33**, 337 (1911); Baxter, G. P., and Parsons, L. W., *J. Am. Chem. Soc.*, **43**, 507 (1921).
- (20) RICHARDS, T. W., AND LEMBERT, M.: *J. Am. Chem. Soc.*, **36**, 1329 (1914); *Z. anorg. Chem.*, **88**, 429 (1914).
- (21) BAXTER, G. P., AND GROVER, F. L.: *J. Am. Chem. Soc.*, **37**, 1028 (1915).
- (22) CURIE, I.: *Compt. Rend.*, **172**, 1025 (1921).
- (23) FARADAY, M.: "Experimental Researches in Electricity," 2nd. ed., vol. 1, p. 195, 1849.
- (24) LORD RAYLEIGH, AND SIDGWICK, MRS. H., SHAW, W. N., KOHLRAUSCH, F., AND OTHERS. Confer. CLARKE, F. W.: *Smithsonian Misc. Coll.*, **54**, No. 3. "The Constants of Nature. Part V. A Recalculation of the Atomic Weights," 3rd. ed., p. 163, 1910.

- (25) RICHARDS, T. W., COLLINS, E., AND HEIMROD, G. W.: *Proc. Am. Acad. Arts Sci.*, **35**, 121 (1899); Richards, T. W., and Stull, W. N., *Proc. Am. Acad.*, **38**, 407 (1902).
- (26) MILLIKAN, R. A.: *Phil. Mag.*, (6) **34**, 1 (1917).
- (27) MALLET, J. W.: *Phil. Trans.*, **171**, 1003 (1880); Cooke, J. P., and Richards, T. W., *Am. Chem. J.*, **10**, 84 (1888); Strutt, R. J. (now 4th Baron Rayleigh), *Phil. Mag.*, (6) **1**, 311 (1901).
- (28) An excellent descriptive compilation concerning this subject, with bibliography, is given in F. P. Venable's book. "The Development of the Periodic Law," Easton, 1896.
- (29) See, for example, Soddy, F.: "Chemistry of the Radioactive Elements," London, 1915, for a correlated exposition of the discoveries of Henri Becquerel, Mme. Marie Sklodowska Curie, Pierre Curie, Sir Ernest Rutherford, Sir William Ramsay, Bertram B. Boltwood and others, as well as for an explanation of the hypothesis of Alexander Fleck, Alexander S. Russell, Frederick Soddy and Kasimir Fajans.
- (30) BOLTWOOD, B. B.: *Am. J. Sci.*, (4) **23**, 77 (1907).
- (31) HILLEBRAND, W. F.: *Am. J. Sci.*, **40**, 384 (1890); Ramsay, W., *Proc. Roy. Soc.*, **58**, 65, 81 (1895); Clève, P. T., *Compt. Rend.*, **120**, 834, 1212 (1895).
- (32) CURIE, M.: *Compt. Rend.*, **158**, 1676 (1914).
- (33) HÖNIGSCHMID, O., AND HOROWITZ, S.: *Compt. Rend.*, **158**, 1796 (1914).
- (34) RICHARDS, T. W., AND WADSWORTH, C., 3RD: *J. Am. Chem. Soc.*, **38**, 1658 (1916). A detailed discussion of the problem of radioactive lead will be found in *Science (N.S.)*, **49**, 1 (1919).
- (35) HÖNIGSCHMID, O., AND HOROWITZ, S.: *Sitz. ber. k. k. Akad. Wiss. Wien*, **123**, (IIb) 1 (Dec. 1914).
- (36) RICHARDS, T. W., AND MERIGOLD, B. S.: *Proc. Am. Acad. Arts Sci.*, **37**, 363 (1902).
- (37) HÖNIGSCHMID, O.: *Compt. Rend.*, **158**, 2004 (1914); *Z. Elektrochem.*, **20**, 452 (1914).
- (38) NEWLANDS, J. A. R.: *Chem. News*, **10**, 94 (1864).
- (39) MOSELEY, H. G. J.: *Phil. Mag.*, (6) **26**, 1024 (1913); **27**, 703 (1914).
- (40) BRÖNSTED, J. T., AND HEVESY, G. VON: *Nature*, **106**, 144 (1920); *Phil. Mag.* (6) **43**, 31 (1922).
- (41) HARKINS, W. D.: *Science (N.S.)*, **54**, 359 (1921); Harkins, W. D., and Mulliken, R. S., *Nature*, **108**, 146 (1921); Mulliken, R. S., *Science (N.S.)*, **57**, 243 (1923).
- (42) BAXTER, G. P., WEATHERILL, P. F., AND SCRIPTURE, E. W., JR.: *Proc. Am. Acad. Arts Sci.*, **58**, 243 (1923); Hönigshmid, O., and Birckenbach, L., *Anales soc. espan. fis-quim.*, **20**, 167 (1922); Baxter, G. P., and Scott, A. F., *Science (N.S.)*, **44**, 524 (1921).
- (43) ASTON, F. W.: *Nature*, **109**, 813 (1922). Since the present essay was written, Aston has found the inexplicable value 88 for Strontium, *Nature*, **112**, 449 (1923).
- (44) CROOKES, W.: *Chem. News*, **54**, 122 (1886).
- (45) PIUTTI, A.: *Z. Elektrochem.*, **28**, 452 (1922).
- (46) RUTHERFORD, E.: *Proc. Roy. Soc.*, (A) **97**, 374 (1920).

- (47) BOHR, N.: *Chem. Weekblad.*, **16**, 621 (1919); *Z. phys.*, **2**, 423 (1920); *Nature* **108**, 208 (1921).
- (48) LEWIS, G. N.: *J. Am. Chem. Soc.*, **38**, 762 (1916); Langmuir, I., *J. Am. Chem. Soc.*, **41**, 868 (1919).
- (49) AMES, J. S.: *Am. Chem. J.*, **11**, 138 (1887).
- (50) DUANE, W.: *Proc. Am. Philos. Soc.*, **61**, 286 (1922).
- (51) LOCKYER, J. N.: *Nature*, **19**, 197 (1879).