

pressed out between white filter papers and dried in the dark. Silk will be colored rose-red by the β -naphthol solution, orange-yellow by the resorcinol, the wool black by both, while the plant fibers will remain white.

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INTER-RELATIONS OF THE ELEMENTS.¹

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The history of chemistry from the first to the sixth decade of the 19th century shows all too clearly how unsuccessful were the attempts of Dalton and of his contemporaries and successors to fix the atomic weights of the elements by means of arbitrary rules regarding the numbers of atoms which unite with one another, even when these rules were supplemented by knowledge of chemical behavior. Consistent results were obtained only by the aid of the auxiliary hypothesis of Avogadro; which, proposed in 1811, almost unappreciated until after its reanimation by Cannizzaro in 1858, to-day is the corner-stone of the magnificent structure of which the atomic hypothesis is the foundation. Between the physical and chemical properties of the elements and their atomic weights, fixed by means of the hypothesis of Avogadro, there are, as is well known to every chemist, the most fundamental relationships. Of these relationships none is perhaps more significant than that discovered in 1819 by Dulong and Petit. This law supplemented by the relations discovered by Neumann and by Kopp means, simply, that for solid substances, the atoms of all elements, either free or combined, have approximately the same capacity for heat. A few months ago Lewis showed that atomic heats at constant volume are much more nearly constant than the ordinary values, which refer to constant pressure.

During the fifty years following Dulong and Petit's discovery many other relations, more or less quantitative, were found between the properties of elements and their atomic weights; all these relationships were correlated, in 1869, in the Periodic Law of Lothar Meyer and Mendeléeff, which may be concisely summarized in the statement that, in general, the properties of elements are periodic functions of their atomic weights. The comprehensive nature of the law is best appreciated when we remember that these properties include chemical nature, valence, atomic volume, hardness, thermal expansion, crystalline form, conductivity for heat and electricity, melting-point, boiling-point, spectral wavelength and ionic mobility, as well as other properties of less importance. What could illustrate more forcibly the validity of this great law than the startling coincidence in properties of the element, germanium, discovered by Winkler in 1886, and the hypothetical eka-silicon described by Mendeléeff sixteen years earlier, or the equally accurate predictions of the same famous chemist concerning eka-boron and eka-aluminium.

¹ Read at the Chicago meeting of the American Chemical Society.

Very early in the history of the atomic hypothesis, in 1815, to be exact, Prout, a London physician and dilettante in chemistry, observed that the currently accepted atomic weights were, for many elements, exactly or very approximately whole numbers, the atomic weight of hydrogen being taken as unity. Prout contended that all atomic weights should be whole numbers and suggested as the explanation that the elements were composed of hydrogen in various stages of condensation. These views were vigorously opposed by many who were best qualified to judge; Berzelius, especially stoutly denied that the fractional values could be wholly due to experimental error. Later, Stas, whose monumental work on atomic weights was largely inspired by a desire to settle this vital question, convinced himself and also the chemical world in general that Prout's idea was fallacious; at least as to the atomic weights being whole numbers. And this conclusion is strongly confirmed by all the beautiful work of more recent years upon atomic weights. Yet the fact that the values found on the basis of oxygen equal 16, are, in so many cases, so very near whole numbers, must have some far-reaching significance. Calculations by Strutt, based on the theory of probability, have shown that the chances are only about one in a thousand that any set of numbers, assigned purely at random, would differ from whole numbers by so little as do the atomic weights.

From the critical consideration of all the evidence of the sort to which reference had been made, one may safely say that there was abundant reason for the belief that the elements are but various modifications of a primitive substance; *but, the case was not yet proven.*

Far from being novel, the idea of the unity of matter, with the attendant possibility of transmutation, antedates the whole science of chemistry. True it is, of course, that the ancient and medieval views had other bases than the facts which we have been considering; was not the transmutation of a base metal into gold a far simpler change (apparently) than many chemical and metallurgical transformations with which men were even then familiar? To the alchemist the argument was convincing and the goal alluring; and with enthusiasm worthy of a twentieth century "promoter" he often, in bombastic and ambiguous terms, described as accomplished that which existed only in his imagination.

Before the close of the 18th century, however, attempts at transmutation were recognized as futile and one thing appeared certain, even at that time; the elements were not to be disintegrated or altered by such chemical processes as those which served to decompose their compounds. Most of the foregoing facts and arguments are well known to every chemist, since they constitute important chapters in the history of our science. I have merely touched upon them in order to lend perspective to that which is to follow.

During the past eleven years enormous advances have been made along entirely new lines, in the knowledge of the interrelations of the elements and the nature of matter. This new knowledge had its origin in the discovery by Becquerel, in 1896, of the radiations emitted by uranium. It was found by Becquerel that all uranium compounds send out rays capable of affecting a photographic plate through light-proof paper and also of enormously increasing the electrical conductivity of air, by ionizing it. Schmidt, and independently Marie Curie, found that all

compounds of thorium produce similar rays. Scientists will never forget the intense interest taken in the discovery by the Curies, of radium, a substance which possessed the properties of uranium and of thorium augmented more than a million-fold. There were also new properties: powerful physiological effects, evolution of light and even of heat, it having been found by Curie and Laborde that the temperature of a tube of radium is always perceptibly above that of its surroundings. Here then was a most marvelous result; the continuous and seemingly undiminished production of energy by a portion of matter, which appeared to suffer no chemical change. It even seemed as if a source of perpetual motion had been found.

It was soon clearly established that the activity of radioactive substances was not due to the excitation of any *known* radiation. Some scientists, however, including Lord Kelvin, Becquerel and the Curies, imagined, as the source of the observed energy an unknown cosmic radiation, which was intercepted and transformed by the radioactive body: the elevation of temperature of radium above its surroundings being, according to Kelvin, analogous to that of a piece of black paper in a bottle exposed to sunlight.

The solution of the mystery of radium is largely due to Rutherford and his colleagues. There were two main problems (1) the nature of the radiations, and (2) the nature and cause of radioactivity. The radiations were found to be of three sorts, called the α -, β -, and γ -rays. The nature of the β -rays was first established. The photoactivity is chiefly due to these rays; they readily penetrate light-proof paper; are easily deflected by a magnetic or an electric field, and in such a direction as to show that they are negatively charged. In this respect, as well as in many others, the β -rays closely resemble cathode rays, which latter have been shown to consist of particles of negative electricity, called corpuscles. These corpuscles, which are shot out from the cathode with $1/10$ of the velocity of light, have inertia, due to the moving electric charge; and having inertia, they have mass. The mass of a corpuscle is very small; about $1/1000$ that of an atom of hydrogen. The β -rays seem to differ from the cathode rays only in having greater velocity. The γ -rays are apparently very penetrating X-rays; and just as the latter are produced by the cathode rays, the former are produced by the β -rays.

The α -rays are quite different: they are unable to penetrate a single sheet of writing paper; but they are the chief cause of the ionization of the air and the elevation of temperature. Rutherford has shown that the α -rays consist of positively charged material particles, each having a mass 2 (or 4) times that of an atom of hydrogen and moving with $1/3$ the velocity of light. It was now readily understood that the kinetic energy of the rays was the proximate cause of the observed evolution of heat by radium.

The counterpart of the phenomena of the rays was found in the change which occurred at the same time in the active substance itself. Crookes had observed that by treating uranium nitrate solution with an excess of ammonium carbonate a minute insoluble precipitate remained; this precipitate, called uranium X, was found to possess practically the whole of the photoactivity of the uranium from which it had been separated. Rutherford and Soddy precipitated thorium with ammonia and obtained

from the filtrate a trifling residue called Thorium X, which possessed a large share of the original activity. The activity of the ThX decreased gradually with time; in 4 days the activity was reduced to $1/2$, in 8 days to $1/4$. The loss of activity occurred according to the exponential law, or, as the physical chemist would say, the change was that of a first order reaction; in each unit of time a fixed fraction of the remaining activity disappeared. To some scientists it did not appear remarkable that the radioactive principle of uranium or thorium could be separated by a chemical process: in fact the original activity of these elements was "explained" as due to the presence of these highly active "impurities." Nor did the loss of activity by UX or ThX, considered by itself, seem extraordinary; it might be likened to loss of temperature by a cooling body.

But a most extraordinary thing was discovered by Rutherford and Soddy, in the further study of this same thorium experiment. The thorium from which ThX had been removed had, at first, only about $1/3$ of its original activity; but in just that measure in which the separated ThX lost its activity, that of the thorium itself returned; until, after a period of several weeks, the thorium had entirely regained its original activity, while the ThX had become inactive. A repetition of the treatment with ammonia now yielded a new portion of ThX equal in amount to that first extracted! The behavior of UX was similar. Rutherford and Soddy then announced their now celebrated Disintegration Hypothesis: the radioactive atom is a complex system, made up of corpuscles and α -particles, in rapid orbital motion; of such systems some, in the course of time, became unstable and disintegrate, the corpuscles and α -particles resulting from such atomic disintegrations constitute the rays, the kinetic energy of which existed previously in the atom. The residual portion of the atom, after the escape of a corpuscle or an α -particle, constituted an atom of a new substance (*e. g.* ThX), which atom might have even less stability than the original.

In all, over 20 distinct radioactive substances are now known. These constitute three series, in each of which each member produces, by its radioactive disintegration, the following member. The evidence in the case of each change is just as clear as in that of thorium and thorium X. One case in particular, that of the formation of radium from uranium, is of especial interest. It has been shown in two different ways that radium and uranium are always associated in minerals, and, moreover, in a perfectly fixed proportion, as demanded by the hypothesis that the one is the product of the other. Further, uranium minerals freed from radium by chemical processes, slowly but surely reproduce the latter substance.

The chemical and physical properties of radium and its salts clearly show it to be a member of the alkaline earth family; its atomic weight is according to the latest determination of Mme. Curie, 226.5, assuming the elements to be bivalent. The formation of radium by uranium was then a clear case of the transmutation of one element into another whatever might be thought of such changes as that involving the production of ThX.

The properties of the α -particle led Rutherford and Soddy to suggest, in 1902, that it might be an atom of helium. In 1903 Ramsay and Soddy

were able to show that radium emanation actually does produce helium in the course of its spontaneous disintegration; this observation has, since then, frequently been confirmed. The formation of helium seemed to be another real transmutation; since the element radium undoubtedly produced the emanation which yielded in turn another element, helium.

If now uranium gives ultimately radium, what is the final product of the disintegration of the latter? Boltwood believes it to be lead, since he finds that all uranium-radium ores contain notable amounts of lead. In the disintegration of an atom of radium five distinct α -ray changes occur. If each produces one α -particle, with atomic weight of 4, the final product of radium should have an atomic weight of $226.5 - 20 = 206.5$, whereas the atomic weight of lead is 206.9.

There is now no shadow of doubt that the rate of radioactive change is entirely independent of the form of chemical combination of a radioactive substance; temperature is also without influence; a given transformation occurs at precisely the same rate at the temperature of liquid hydrogen and at white heat. It thus appears that radioactive change is a natural process which is entirely beyond man's control, and important as is the establishment of this fact, the discovery falls far short of being a complete solution of the problem of the transmutation of the elements.

A further step in this direction seems to have been taken within the past few months, however, by Sir William Ramsay. The alchemist in his attempts to alter the elements, could apply only the forces of moderate heat and chemical affinity. The chemist of the 19th century could command enormously greater ranges of temperature as well as powerful electrical forces; all these means were likewise without avail. And now Ramsay has tried a new force, that of radioactive radiations: corpuscles and particles of matter, both electrically charged, projected with almost inconceivable velocity. The results of the experiments of Ramsay and Cameron may be stated very briefly; radium emanation acting on water produces neon; while with a solution of copper nitrate it produces argon; and even the copper itself appeared to be attacked, for when the latter element was removed by means of hydrogen sulphide, the filtrate was found to contain lithium. A blank experiment, in which the radium emanation was omitted but all other conditions remained precisely the same, yielded no trace of lithium. The formation of lithium from copper has been observed four times by Ramsay and though, as he writes in a private communication, "he was loth to believe," yet he "had to chronicle the results after four repetitions." The importance of these facts, provided they are not due to some spurious cause, needs no comment. In this connection it occurred to me that radium emanation, or in general radioactive radiations, might act on copper in the solid state; if so, uranium-radium minerals which contain copper should contain lithium also. For another purpose I had, more than a year earlier, separated a sample of pitchblende into its principal constituents. There was a considerable quantity of copper; there was also a solution which could contain only alkali and ammonium salts. It was but the work of an hour to examine this solution for lithium; in the spectrum the characteristic red line of lithium was next in brilliancy to that of sodium! Later, from one to two grams of four other uranium minerals, including sam-

ples of pitchblende, carnotite and gummite, from widely separated localities, were examined for copper and lithium: all contained lithium and all but one contained copper. The presence of lithium in a mineral free from copper may be explained upon the supposition that the transmutation of the latter metal had been completed.

The view that the atom is a complex system made up of negatively charged corpuscles and positively charged α -particles has been made the subject of extensive mathematical studies by J. J. Thompson. Thompson's hypothetical atom is a system composed of rings or shells of corpuscles in a uniform sphere of positive electrification. The electropositive or negative nature of atoms, their chemical affinity as well as their dual valence toward hydrogen and oxygen are all most beautifully and at the same time simply explained by the behavior of such imaginary systems, the properties of which vary periodically with increasing number of corpuscles and so fulfil another indispensable requirement of any hypothetical atom. Numerous other properties of matter also receive a satisfactory explanation in terms of the new hypothesis: among such are the conductivity of metals for heat and electricity, bright line spectra and the Zeeman effect. That the corpuscular theory is the last word on the nature of matter, none will contend: Thompson himself writes, "The theory is not an ultimate one; its object is physical rather than metaphysical. From the point of view of the physicist, a theory of matter is a policy rather than a creed; its object is to connect and coordinate apparently diverse phenomena, and above all to suggest, stimulate and direct experiment."

The view just given of the nature of the atom accounts also for its radioactivity. A system of revolving corpuscles of negative electricity would slowly radiate energy, at an almost infinitesimal rate it is true; but the final result would be to produce in the system a condition of instability which would cause its partial disintegration and rearrangement. Is then all matter undergoing evolution? That is the question which cannot be positively answered at present. And yet there is much evidence that many elements are faintly radioactive. Such activity may be either intrinsic or due to minute amounts of known highly active substances. Radioactive matter is easily extracted from the air by means of a negatively charged wire exposed out of doors, as first shown in 1901 by Elster and Geitel. The rate of change of this active matter indicates that it is chiefly the excited activity, Ra A, B and C, resulting from the disintegration of radium emanation. A simple experiment which I recently tried shows the correctness of this view. Air was liquefied and about a liter of the liquid was allowed to evaporate, and the last portion was examined for radioactive emanations. A considerable activity was found, the rate of change of which plainly indicated the presence of radium emanation together with small amounts of other active matter. The excited activity, which is deposited everywhere by the radium emanation contained in the air, is certainly the cause of a portion of the observed activity of common things. Nevertheless, at least one common element, potassium, seems from the studies of Campbell to possess slight intrinsic activity.

On the other hand, it is found that α -particles having less than a certain minimum velocity are unable to produce ionization of the air. It

is therefore quite possible that some atomic transformations may occur which do not show radioactive phenomena, the initial velocity of the α -rays being, in such cases, below the minimum. Such change might occur at rates far greater than that of uranium and still be impossible of detection in the course of a lifetime by gravimetric or even probably by spectroscopic methods, since in the case of uranium the rate of change is so slow that no more than 0.001 per cent. disintegrates in 10,000 years; and yet the ionization method of recognizing α -radiations is so surpassingly delicate that one may detect with certainty the activity due to a single milligram of uranium in any form of combination!

In conclusion, it may be said that while the work of the 19th century produced abundant and varied evidence that between the elements there exists the most intimate interrelationships, the researches of the past few years of this new century have shown the fundamental significance of these relationships and lead us to the conclusion that the elements may no longer be considered immutable; that matter is probably of but a single sort, of which our commonest elements represent the more stable forms, which have resulted from a process of natural evolution.

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CORRECTION.

Plot and footnote omitted by mistake from article on "The Corrosion of Iron and Steel," by W. H. Walker, A. M. Cederholm and L. N. Bent, in September number of this Journal, 1907. The plot should be inserted to

