

# SCIENCE

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## CONTENTS:

<i>The Revival of Inorganic Chemistry:</i> DR. H. N. STOKES, .....	601
<i>On the Total Solar Eclipse of May 28, 1900:</i> PROFESSOR TRUMAN HENRY SAFFORD.....	615
<i>Reception and Exhibition of the New York Academy of Sciences:</i> PROFESSOR WILLIAM HALLOCK..	616
<i>Scientific Books:—</i>	
<i>Campbell on the Evolution of Plants:</i> PROFESSOR CHARLES E. BESSEY. <i>Groos's Die Spiele der Menschen:</i> HIRAM M. STANLEY. <i>Books received</i> .....	618
<i>Scientific Journals and Articles</i> .....	620
<i>Societies and Academies:—</i>	
<i>The National Academy of Sciences. The Philosophical Society of Washington:</i> E. D. PRESTON. <i>Geological Society of Washington:</i> DR. W. F. MORSELL. <i>Chemical Society of Washington:</i> DR. W. H. KRUG. <i>Minnesota Academy of Natural Sciences:</i> CHARLES P. BERKEY. <i>The Academy of Sciences of St. Louis:</i> PROFESSOR WILLIAM TRELEASE. <i>Boston Society of Natural History:</i> SAMUEL HENSHAW .....	621
<i>Discussion and Correspondence:—</i>	
<i>The Action of the Coherer:</i> M. F. LOCKWOOD, E. B. WHEELER. <i>Two-Headed Snakes:</i> ROWELL H. JOHNSON. <i>Duplication of Geologic Formation Names:</i> F. B. WEEKS .....	624
<i>Notes on Inorganic Chemistry:</i> J. L. H.....	626
<i>Current Notes on Meteorology:</i>	
<i>Frost Prediction and Protection; A Fog Dispeller; Notes:</i> R. DeC. WARD.....	627
<i>Scientific Notes and News:—</i>	
<i>The American Association for the Advancement of Science; Geological Survey Work in Alaska:</i> W. F. M. <i>Scientific Positions under the Government; General</i> .....	628
<i>University and Educational News:—</i>	
<i>Assistants in Physiology in Harvard Medical School; General</i> .....	631

## THE REVIVAL OF INORGANIC CHEMISTRY.\*

NOTHING can be more instructive to the student interested in the results of intellectual cross-fertilization than the effect of the recent fecundation of chemistry by physics. Through the application of physical methods and ideas to chemistry, the latter has given birth to a new branch of study, physical chemistry, which promises to produce as radical a change in our conceptions of molecular phenomena as did the overthrow of the phlogiston theory or the introduction of the conception of valency at a later period.

The attempt of Berthollet to introduce dynamical conceptions into chemistry, at the beginning of the century, fell on thorny ground, and from that day until very recent years the growth of chemistry, great as it has been, has been most remarkably one-sided. The Periodic Law has been discovered, many new elements have been found, new compounds without number have been prepared, the rules governing their formations and transformations have been ascertained, and even their microscopic anatomy has been studied to such an extent that for countless of them we have established formulas which express, schematically, the relative arrangement of the atoms in the molecule. In stereochemistry we have even gone so far as to be able to

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indicate, in a rough way, the actual relations of the atoms in space; yet, with all this, a most important part of the problem has been almost neglected. To use a biological expression, chemistry has been enormously developed on the morphological, and but little on the physiological side. Chemists have concerned themselves greatly with the products of chemical reactions, and but little with the nature of the reactions themselves. The molecule has been treated as a dead, rigid body is treated by the anatomist, but its study as a living, moving mass, filled with energy and capable of reacting by virtue of this energy, has been largely left to the future. Even as late as 1882 the German physiologist Emil du Bois-Reymond used the words which have since been in the mouth of every physical chemist:

"In contradistinction to modern chemistry, we may call physical chemistry the *chemistry of the future*."

Since 1882, thanks to the labors and inspiring influence of Ostwald, van't Hoff, Arrhenius, Nernst and others, physical chemistry is no longer the chemistry of the future merely, but of the present, and apart from the quickening influence which it is exerting in nearly all branches of chemistry proper, both pure and applied, we are beginning to perceive that we are entering a period in which chemistry will be of greater service to the allied sciences. Geological chemistry is showing signs of reviving under the stimulus of physico-chemical conceptions, and we are finding, too, that as physiological chemistry is not merely the chemistry of sugar, or urea, or albumin, but preeminently a science of moving and changing molecules, it can only progress by the aid of a knowledge of the laws of chemical energy.

The achievements of physical chemistry form, perhaps, the most interesting phase of the recent history of our science, but its

followers have spoken for themselves so often of late years, and have presented the subject so much better than I could do it, that I feel compelled to consider a perhaps humbler, but yet not unimportant, field of research, which, in a sense, may also be called a part of the chemistry of the future, the field of *Inorganic Chemistry*. The relations of physical and inorganic chemistry have recently been discussed by van't Hoff in his admirable address delivered last summer before the Society of German Scientists and Physicians, and I shall, therefore, limit myself to the consideration of a few points of a more strictly chemical nature, touching the relations of physical and inorganic chemistry only incidentally.

The aim of physical chemistry will have been accomplished when it has established a mathematical equation which, by proper substitution, will enable us to predict the nature of every possible chemical system or reaction, and the properties, physical and chemical, of every possible element or compound. Until he has reached this chemical millennium, unless he will risk falling into the pit which has received so many philosophers in the past, the chemist must continue to advance by the route by which our understanding of every other branch of physical science has been reached. Notwithstanding all that physical chemistry can do with this material at present in hand, the experimenter must long continue to take the short cut to knowledge and find out what his elements and compounds will do by first actually getting them in hand, by precipitation, filtration, distillation, crystallization and the like. It may be questioned whether our present knowledge of facts would ever suffice to enable us to predict, for example, a single atomic weight with accuracy, or to explain that wonderful relation between properties and atomic weights known as the Periodic Law. A few enthusiastic physical chemists have

spoken slightly of the compound-maker, as a kind of inferior being, apparently forgetting that it is just this kind of pioneer work which has supplied the material for their labors, that the first requisite for successful generalization is the possession of a large number of pure substances, of accurately known composition and properties, many of which can only be obtained by work which is so elaborate and difficult, and which requires such concentration of effort that he who follows it can well be excused if he does not always look on the product of his labor as merely means to another end. It is tolerably clear that, for a long time to come, experimentizing must keep equal pace with mathematicizing, and if the former have been pushed so far in one direction as to appear to afford no prospect of continued progress we must not abandon it altogether, but consider whether it may not be still profitably pursued along other lines. Let us consider whether we must all turn mathematical chemists, or whether there is not much left to be done by those trained in the older school, working along old-fashioned lines and by old-fashioned methods.

Descriptive chemistry, as it exists to-day, is a science which has grown and is still growing enormously in a single direction, that of organic chemistry, the chemistry of the compounds of carbon. We are at present acquainted with about seventy-five chemical elements, which are found in the most varied proportion in those parts of the earth which are accessible to our observation, namely, the crust, the sea and the air. The accompanying table, calculated by Clarke, shows the relative abundance of the elements in a sphere comprising the crust for a depth of ten miles, the ocean and the atmosphere :

Oxygen .....	49.98
Silicon.....	25.30
Aluminium.....	7.26
Iron .....	5.08

Calcium .....	3.51
Magnesium.....	2.50
Sodium .....	2.28
Potassium .....	2.23
Hydrogen .....	.94
Titanium.....	.30
Carbon .....	.21
Chlorine } .....	.51
Bromine }	
Phosphorus.....	.09
Manganese .....	.07
Sulphur.....	.04
Barium .....	.03
Nitrogen .....	.02
Chromium.....	.01

The nineteen elements here given make up nearly the whole mass ; the remaining fifty-five or thereabouts, taken together, and making all possible allowance for error, do not amount to more than at most 1 per cent. Observe that the element *carbon* amounts to but one-fifth of 1 per cent. To be sure, this is no argument that the chemistry of carbon is relatively unimportant ; on the contrary, there is no necessary connection between the abundance of an element and its ability to carry us further toward a knowledge of chemical laws. Nevertheless, to an intelligence not having its seat in a body largely made up of carbon compounds, it might appear somewhat surprising that chemists should have attempted to base a science on the investigation of an element which exists in such relatively insignificant amounts, the compounds of which, with but few exceptions, are incapable of formation at the freezing point of water, or of existence at the lowest red heat ; and should have chosen to devote nearly all of their energy to its study.

Apart from the special subject of coal, petroleum and asphalt, carbon is of practical importance to the geologist only in the form of carbon dioxide and the carbonates, while of the chemical properties of silicon, which constitutes 27 per cent. of the earth's crust, and of the silicates, which make up nearly all of it, we know vastly less than of the

derivatives of the single carbon compound, *benzene*. A study of the chemical changes taking place in the sun, and of most of those occurring in the interior of the earth, might almost leave carbon out of account; it would certainly have no more importance than titanium, an element of which few but chemists have ever heard, but which is more abundant and as widely distributed.

Carbon, as an essential constituent of living beings, constantly forces itself on our attention, yet this is not to be considered as by any means the chief cause of the predominance of organic chemistry. Comparatively few of the best studied organic compounds have more than the remotest connection with the phenomena of life. Phosphorus and sulphur, to say nothing of oxygen, hydrogen and nitrogen, are quite as important in this respect as carbon, yet how relatively little do we know of phosphorus and sulphur in their chemical relations, or even of nitrogen. The extraordinary development of carbon chemistry is due mainly to reasons of a chemical nature, which, by rendering its compounds easier to study, have made progress in this direction a line of least resistance. This has not been without its advantages, for we have been led to discern laws which could not have been perceived so soon had the working forces been more evenly distributed, but it has also had the unfortunate result that the theories of molecular structure, derived wholly from the study of carbon compounds, have been applied to all classes of inorganic compounds too hastily and without sufficient research. The inorganic chemist has done little but make new compounds, and ascribe to them structural formulas seldom based on the results of experiment, but rather on the possibility of drawing schemes on paper, in which the various valences or bonds were mutually satisfied (how, did not matter much), while those substances which were inconsiderate

enough to refuse to submit to this operation without violating every probable or possible assumption have been labeled 'molecular compounds,' and under this name submitted to a forced neglect, which soon resulted in their being forgotten. We shall presently see that an increasing respect for these so-called molecular compounds is one of the features of the revival of inorganic chemistry.

In the earlier days of chemistry no sharp line was drawn between inorganic and organic substances. It is generally thought that we owe this distinction to Nicholas Lémery, who, in 1675, classified substances, according to their origin, as mineral, vegetable and animal, a distinction which has survived until the present day in popular speech. Lavoisier, recognizing in substances of vegetable and animal origin the elements carbon, hydrogen, nitrogen and oxygen, and led by his researches to attribute a peculiar importance to oxygen, regarded inorganic bases and acids as oxides of simple radicals, and organic bodies as oxides of compound radicals composed of carbon, hydrogen and sometimes nitrogen, but did not otherwise distinguish them. Even in 1811 it was undetermined whether carbon compounds obey the laws of constant and multiple proportions, and it was two or three years more before Berzelius, having sufficiently improved the methods of organic analysis, definitely proved that they do, in fact, conform to these laws, but are of greater complexity than the comparatively simple inorganic compounds then known. In his electro-chemical theory, the theory of dualism, developed between 1812 and 1818, Berzelius regarded the simple inorganic bodies, such as the bases and acids, as binary compounds of positive with negative atoms, held together by electrical attraction; the more complex bodies, as the salts, being binary compounds of a higher order; the organic compounds, on the contrary, being

regarded as ternary or quaternary. Later he extended the dualistic conception to these also, adopting the idea of Lavoisier that they are binary compounds of oxygen with compound radicals, composed of carbon, hydrogen and sometimes nitrogen, a view which he developed further and never wholly abandoned. In 1817 we find Leopold Gmelin maintaining that organic compounds are the products of a vital force and cannot be produced artificially. This view was entertained by Berzelius even as late as 1827 or later. Berzelius attributed the formation of organic compounds, with their relatively weak positive and negative characters, to peculiar electrical conditions existing in the organism. We cannot reproduce these conditions in the laboratory, and, therefore, cannot produce organic compounds artificially. Those transformations which we are able to effect are always from the more complex to the simpler. We can isolate the intermediate stages in the breaking-down of organic matter into carbon dioxide, water and ammonia, that is, we can follow the change of matter from the organic to the inorganic, step by step, but we cannot reverse the process and build up, nor can we hope to do so in the future. This opinion of Berzelius marks the widest gulf between organic and inorganic chemistry, a gulf too wide for human power to bridge. How dangerous it is to set limits to the power of science! But one year later, in 1828, Wöhler announced his discovery that urea, a body of animal origin, could be produced from ammonium cyanate, a substance, which, in its turn, can be built up from its constituent elements, carbon, hydrogen, oxygen and nitrogen. This was the first of a series of innumerable syntheses which have fully disposed of the idea that any fundamental distinction exists between inorganic and organic compounds. Although we have not yet made albumin in the laboratory, we all expect that it will be done,

and nearly every chemist now believes that even the properties of living protoplasm are due, not to any peculiar vital force inherent in the protoplasm itself, but to the special properties of the carbon, hydrogen, oxygen, nitrogen, phosphorus and other elements of which it is composed. My subject does not permit me to consider in detail how the idea of organic chemistry, as the chemistry of compound radicals, was evolved; how the radical theory was replaced by the conception of the molecule as a unit; how, in 1853, the theory of valency began to develop, and how this, with the type theory, the theory of the linkage of atoms, and the constant tetravalency of carbon, led, in the early sixties, to our present conceptions of the structure of organic molecules. With the advent of the fully developed structural formula, the brilliant progress of organic chemistry toward fuller theoretical development came to an end with remarkable suddenness. Kekulé's ingenious and fruitful theory of the benzene ring, suggested in 1865, was an application, to a particular class of compounds, of principles already established, but involved no fundamentally new conceptions. Organic chemistry entered upon what has aptly been termed a period of 'formula worship.' The establishment of the constitutional formula became the highest aim of the devotees of this cult, against which but few chemists, for example, Kolbe and Mendelejeff, have had the courage to protest. In pursuing this aim the organic chemists have unquestionably accumulated an enormous mass of valuable information and detail; have discovered new methods of synthesis, new laws of more or less special application and new compounds of practical value; but, with all their labors, the ordinary structural formula of to-day means no more than it did in 1865. In stereo-chemistry, however, the development of the structural formula in space of three dimensions, organic chem-

istry, has shown real progress, especially since 1887, when LeBel and van't Hoff's theory of the asymmetric carbon atom, which was proposed in 1874, but which slumbered almost forgotten, was revived by Wislicenus. At present the most important developments of structural chemistry, both organic and inorganic, unquestionably have the question of space relation as their basis.

The development of inorganic chemistry presents some marked distinctions from that of organic chemistry. Up to the year 1820 nearly all the important discoveries and generalizations came from the inorganic side. Richter's discovery of the law of equivalents; the researches of Scheele, Cavendish, Priestley; the development of the theory of oxidation by Lavoisier; the atomic hypothesis of Dalton and his laws of constant and multiple proportions, and the placing of them on a firm foundation by the remarkable labors of Berzelius; Gay Lussac's law of the simple relation of the volumes of reacting gases; Dulong and Petit's law, and the law of isomorphism, all fall within this period and antedate the beginning of the rapid development of carbon chemistry. The same is true of the discovery of the alkali metals, the recognition of the elementary nature of chlorine, and of the establishment of the existence of hydrogen acids, and many other important facts. In these the study of carbon played a relatively insignificant part. The electro-chemical theory of Berzelius, too, which was of such great importance as a working hypothesis, was of inorganic origin. By 1830 the predominance of organic chemistry was already pronounced, and with the increased attention given to this new field the interest in inorganic chemistry lagged behind. All, or nearly all, the developments of theoretical importance began to come from the inorganic side. The history of chemistry from 1830 to 1865

is practically the history of organic chemistry. I do not mean that research was confined merely to carbon compounds. The influence of Berzelius continued to be felt, and men like Heinrich Rose, Wöhler, Bunsen and many others made valuable contributions to inorganic chemistry, as well as several like Dumas, Liebig and others, whose reputation rests chiefly on their organic work. The great inorganic chemists were mostly men of an analytical rather than synthetical turn of mind. The growth of mineralogy led to the discovery of new elements, and the analytical requirements to which it, as well as practical chemistry, gave rise conduced largely to the study of inorganic compounds. The conception of valency, while due mainly to organic chemistry, owes not a little to inorganic chemistry, though it did but little to further it. Numerous atomic weight determinations of greater or less accuracy were made, sometimes with a purely analytic purpose, sometimes with the object of testing the validity of Prout's hypothesis, but these exercised but little influence on the theoretical growth of inorganic chemistry, which remained for the most part a mass of unconnected facts.

In considering the causes to which is due the preeminent attention given to organic chemistry since 1830, the point most to be emphasized is that at no time since that date has there been lacking a well-defined working hypothesis of the nature of organic compounds. Not only did these substances prove eminently susceptible of classification into types, but, for reasons to be stated later, the transformations discovered were so numerous, and the possibilities of producing synthetically old or new compounds, and of working out new theories, were so attractive that most of the best chemical minds between 1830 and 1865, or even later, were drawn into organic chemistry. Another important factor is that of inertia. Most students of nature do not willingly

enter upon entirely new fields of research. The pupils of the great masters of organic chemistry, Liebig, Dumas, Hofmann, Wurtz, Kolbe, Kekulé and others, found enough to do in following in the footsteps of their teachers, and were little inclined to seek new pastures. The requirements of candidates for the doctorate, whereby the experimental material for the dissertation had to be accumulated in a comparatively short time, led to the assignment of topics with which the instructor was familiar, and which were fairly sure of giving positive results within a year or two, and, as we all know, no branch of chemistry yields results so readily as the study of carbon compounds, with its highly developed synthetical methods. As the *Chemiker-Zeitung* has recently pointed out, even at the present day the full professorships in German universities are almost invariably held by organic chemists, while inorganic chemistry is left to subordinates. The weight of authority and influence being on the side of organic chemistry, the student who looks forward to a university career sees that his chances of promotion are better if he follow the organic rather than the inorganic direction. I need hardly add that the more mercenary hope of obtaining a new dye-stuff or a new remedy, or of replacing nature in making an alkaloid, has also been a powerful incentive to many.

Let us now consider some of the reasons which have their root in the chemical peculiarities of carbon, and which render its compounds, at least those which are not too complex, comparatively easy to study. These conditions are not peculiar to carbon, but no other element, as far as is known, presents as many of them at the same time.

1. Carbon compounds being very generally soluble in neutral solvents, frequently crystalline, and often volatile without decomposition at comparatively low temperatures, are peculiarly adapted to separation

in a state of purity by fractional crystallization or distillation, and for the same reason it is usually possible to determine their true molecular weights. The very general possession of melting or boiling points lying within easily observable ranges of temperature greatly facilitates identification.

2. The power of carbon of uniting, atom to atom, to form chains, the form and size of which can be easily regulated by known synthetic methods, and the stability of which is sufficient to allow of manipulation under easily attainable conditions, is a marked peculiarity of this element. This, with the power of forming stable compounds with hydrogen, is the basis of the definition of organic chemistry as 'the chemistry of the hydrocarbons and their derivatives.' With regard to self-linking power the other elements are in marked contrast. We know with certainty no compounds in which two atoms of boron are linked, not more than four nitrogen atoms have been arranged tandem, while of silicon, the nearest relative of carbon, we know at best a half-dozen well-defined compounds with two atoms of this element in series, and but one with three; analogues of the hydrocarbons are unknown, with the exception of silico-methane, and the instability of this is sufficient proof that a series of silicon paraffines would be most difficult to prepare, and the same would apply to all classes of silicon compounds in which self-linking is a prerequisite. It does not appear probable that we shall ever have a very extensive chemistry of the 'hydrosilicons and their derivatives.' Among the compounds of other elements self-linkage occurs in but few cases and is limited in extent.

3. It is a highly important property of carbon compounds that their molecules tend to preserve their individuality; they generally do not, though there are exceptions, *spontaneously* avail themselves of opportuni-

ties for condensation, whether by polymerization or by union of two or more molecules with separation of water or ammonia. The so-called double and triple union between carbon atoms only exceptionally leads to spontaneous polymerization, while with silicon this latter is apparently the rule. The important carbonyl group,  $C=O$ , the characteristic group of organic acids, aldehydes and ketones, shows but little tendency to polymerize, while organic hydroxyl compounds are usually stable and do not spontaneously give rise to ethers or acid anhydrides. The silicon analogue of carbonyl,  $Si=O$ , on the contrary, appears to polymerize with great ease. The ethers of carbonic acid are well known, but the metasilicic ethers, those of the type  $SiO(OR)_2$ , appear to exist only as polymers. The silicic acids, too, show a marked tendency to condense by dehydration and pass spontaneously into complex bodies. It is easy to see what would have been the result if carbon behaved like silicon. Instead of the innumerable sharply defined organic acids, aldehydes, ketones and alcohols, each produced by a definite synthetic process, each reaction would give rise to an almost inextricable mixture of condensation products, carbon dioxide would be a solid like silica, and organic chemistry would be scarcely further advanced than is the chemistry of silicon. This tendency of carbon compounds to simplicity in reaction, each molecule acting as if it were alone present, has been, therefore, an important factor in facilitating the growth of organic chemistry.

4. Another feature of carbon, which plays an important part, is the ease with which intermediate or transition products can be formed. It is much easier to limit reactions in the case of carbon compounds than in others. Compare, for example, the action of chlorine on  $CH_4$  and  $SiH_4$ .

5. The tendency to dissociation, both hydrolytic and electrolytic, is in general less

marked among carbon compounds, whence it is easier to control the course of a reaction and to exclude changes of a spontaneous nature. Finally, the carbon compounds show but little tendency to the formation of so-called molecular addition products, of which the metal ammonias, the double salts and the compounds with water of crystallization are examples, the rational interpretation of which is difficult.

A full consideration of the peculiarities of carbon which have facilitated the synthesis of such vast numbers of organic compounds would be beyond the scope of this address. The above are the most important, and their relative absence in the majority of elements explains largely the backward state of our knowledge of them. Our inability to determine the true molecular weight of insoluble and non-volatile substances; the difficulty of limiting reactions so as to obtain intermediate products; of preventing condensations; of separating mixtures and identifying their constituents by such simple methods as melting- and boiling-point determinations; of building up step by step; of dissecting atom by atom; of explaining molecular compounds—these are hindrances which can only be overcome by greater perfection of our experimental methods, and which often render the study of the constitution of inorganic bodies a problem of great difficulty, even in the case of many of the simplest.

At the very time that the organic structural formula was beginning to turn the attention of organic chemists away from a further development of theory to a greater elaboration of details the Englishman Newlands was publishing papers which contained the germ of the Periodic Law. In 1865 Kekulé announced his theory of the benzene ring; in 1864 Newlands showed that if the elements be arranged in the order of their atomic weights 'the eighth element, starting from a given one, is a kind



of repetition of the first, like the eighth note of an octave in music.' This discovery of Newlands of a fact which later developed into the Periodic Law does not, however, mark the beginning of a new direction in chemical thought. It marks rather that point in a long series of speculations at which chemists were beginning to grasp an idea after which they had been groping blindly for many years, the conception that the elements are not wholly unrelated bodies, but that there is some definite law connecting their properties with their atomic weights. Beginning in 1815, with the claim of Prout that the atomic weights of the elements are multiples of that of hydrogen, which led him to suggest that hydrogen is the primitive element from which the others are built up, we find numerous speculations, some devoted merely to finding arithmetical relations among the atomic weights, such as the law of triads, others attempting to show how the elements could be built up from one or more primitive constituents. Most of these did not lead to any marked advance of chemical theory, but Prout's hypothesis found very able defenders and greatly encouraged accurate atomic-weight determinations. The labors of Dumas, Marignac and especially of Stas, in this field, are directly due to the desire to test the validity of Prout's suggestion. Up to 1860 not only were the atomic weights uncertain to within a few decimals, but, for other reasons, even the relative position of the elements in an ascending series was often uncertain; our present empirical formulas had not been fully established; it was uncertain, for instance, whether water was  $\text{HO}$  with  $\text{O} = 8$  or  $\text{H}_2\text{O}$  with  $\text{O} = 16$ , or whether silica was  $\text{SiO}_2$  with  $\text{Si} = 28$  or  $\text{SiO}_3$  with  $\text{Si} = 21$ . So when Gladstone, in 1853, arranged the elements in the order of ascending atomic weights he failed to perceive any noteworthy relation. Nine years later the

French engineer and geologist de Chancourtois, using the newer and now adopted atomic weights, arranged the elements in a spiral or helical form around a cylinder, in ascending order, and was led to the conclusion that the 'properties of bodies are properties of the numbers,' a vague statement of the now familiar phase that the properties of the elements are functions of their atomic weights. As already mentioned, he was followed closely by Newlands, whose work, however, met with but slight recognition. Time is wanting to show how in the period 1864-1869 the Periodic Law was developed by the labors of Newlands, and more especially of Lothar Meyer and Mendelejeff, working independently. It affords an interesting example of how a great idea is developed about the same time in the minds of several men working independently and unknown to each other. In 1871 Mendelejeff published a table which shows the periodic law essentially as we find it to-day, the only changes consisting in the addition of a few newly discovered elements and in placing a few of the older elements in their proper positions, as a result of more accurate atomic-weight determinations.

The period 1863-1870 was, therefore, of the greatest importance for inorganic chemistry, as it saw the development of the idea that the properties of the elements are *periodic* functions of their atomic weights. The time which has since elapsed has been even more fruitful than any previous period in speculations, having for their object the finding of mathematical relations between the atomic weights and in theories of the evolution of matter from one or two primal constituents. Many modifications of the periodic scheme have been devised, but they present but few or no advantages over the simple arrangement of Mendelejeff and Lothar Meyer. The great fact still remains, unmodified and unimproved, that if the ele-

ments be arranged in the order of increasing atomic weights there is a recurrence of the properties of elements lower in the scale—in short, that these properties are periodic functions of the atomic weights.

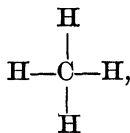
The discovery of the new group of inert gases, helium, neon, argon and xenon, with perhaps krypton and metargon, has not modified our idea of the Periodic Law essentially. They appear to fit well into the system, and it is now only remarkable that their existence was not surmised by Mendeleeff, who so successfully predicted several then-unknown elements. Although the periodic system is, even to-day, the object of attack by a few chemists, who appear to be blinded by its unquestioned defects to the obvious truths which it expresses, it may be safely said that the great central fact of the periodicity in the properties of the elements is just as firmly established as the law of gravitation, and that, whatever modifications may have to be made in the scheme as a whole, this central fact will never be done away with. The atomic theory may be supplanted by something better, but its successor will equally have to take account of the stoichiometrical relations of the elements, which are based not on theory, but on observation pure and simple, and it is on these, and not on the atomic theory, that the Periodic Law is based.

The Periodic Law is exerting a stimulating influence on inorganic chemistry in various ways. It is leading to a more careful study of all the elements, with the object of discovering further analogies; new compounds are being prepared and old ones studied better with this in view; new kinds of periodicity are being sought for in physical as well as in chemical properties. The question of the nature of the rare earth metals, the asteroids of the elementary system, as Crookes calls them, is being attacked with greater energy. Are these, of which Crookes claims there are thirty or

perhaps sixty, capable of being fitted into the system, as it now exists? Must we modify it in order to take them in, or do they represent certain exceptional phases of the evolution of matter from the original protyl, or different very stable modifications or allotropic forms of a few elements? Do the blanks within the system represent existing but as yet undiscovered elements? Do some of them correspond to hypothetical elements which for some unknown reason are incapable of existence, like many organic compounds which are theoretically possible, but which, if momentarily existing, lapse at once into other forms, or must the scheme be so modified as to exclude them? These are some of the questions raised by the Periodic Law which it belongs to the inorganic chemist to solve. Most important of all is the question of the *cause* of the periodicity. Before we can hope to establish a mathematical and possibly a genetic relation between a series of numbers, such as the atomic weights and the chemical properties of the elements, we must establish with greater accuracy than heretofore the precise magnitude of these numbers, and it is this that an ever increasing number of atomic-weight chemists is striving to do. The question of the unity of matter is one to a solution of which we are no nearer than ever, and the Periodic Law, in its present form, does not afford a proof or, I think, even a presumption in favor of a genetic relation between the elements. It is quite conceivable that we may have relations of properties without a common origin. With ever increasing accuracy, we seem to be removing further and further from the possibility of any hypothesis like that of Prout. The electric furnace, with its temperature of  $3,500^{\circ}$  C., gives not a sign of the decomposition or transformation of the elements. These questions and the query why we know no elements below hydrogen or above uranium, why the num-

ber of the elements is limited, and why there are not as many kinds of matter as there are different wave-lengths of light—all these seem to belong as yet to a scientific dreamland rather than to the realm of legitimate research, yet their solution, if possible at all, will be accomplished only by the labors of the inorganic chemist.

Let us now turn to the more special consideration of the questions of the constitutional formulas of inorganic compounds. The more conservative organic chemists have always been careful to state that the so-called structural formulas are *reaction formulas* merely, that is, that they are not intended to express the actual relations of the atoms in the molecule, but are merely convenient schemes for rendering possible reactions visible to the eye. Probably most chemists regard them as more than this, as actual diagrammatic representations of the way in which the atoms are combined. The formula of marsh gas, for example,

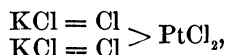


is regarded as more than a visualizing of its chemical properties; it implies that the carbon atom is an actual physical link between the hydrogen atoms, which are combined directly with the carbon but not with each other. Stereochemical formulas are confessedly more than reaction formulas, and the steric conception of the so-called double and triple union asserts that these actually exist in the sense the words imply, and are not merely names for unknown conditions.

Many of the simpler organic structural formulas unquestionably have an enormous mass of evidence in their favor, but many others we must be on our guard against taking too seriously, and must for the present regard as nothing more than reaction

formulas. That we can regard any of them as well established is due, more than to anything else, to the almost invariably constant tetravalency of the carbon atom. Unfortunately, the valency of many of the elements entering into the composition of inorganic compounds appears to be extremely variable and uncertain, and this has greatly impeded the study of the structure of these bodies. The inorganic chemist has been far too prone to assume that the structural theories of the organic chemist are of universal applicability, and, having once for all attributed a certain valency to an element, has been often content with devising structural formulas which have no better claim to recognition than that all the so-assumed bonds are 'satisfied.' At other times a particular valency has been assumed for no other reason than that it enabled him to contrive a formula for the special case under consideration. The books treating of such matters frequently exhibit wonderfully ingenious inorganic structural formulas which are wholly devoid of a reasonable amount of experimental evidence and which are, therefore, often nothing but pure rubbish. With many inorganic chemists, formula worship has degenerated into fetishism. Let us consider a few examples. For nitric acid, one of the simplest and most familiar inorganic compounds, several constitutional formulas may be written, in which the hydrogen is directly united to the nitrogen or separated from it by one or two oxygen atoms, and in which nitrogen may be either tri- or pentavalent. Some of these are given in the books as if they were gospel truth. Brühl, who has investigated the question by physical methods, suggests that the hydrogen atom is not directly united to any part of the  $\text{NO}_3$  radical, but is rotating around it and possibly combined with each oxygen atom in succession, a view approaching that of Werner. There are at least five formulas

proposed for this simple acid. For the familiar potassium chloroplatinate,  $K_2PtCl_6$ , there are four constitutional formulas seriously advocated at present. It may be  $K_2 = PtCl_6$ , with octavalent platinum;



with tetravalent platinum and trivalent chlorine, as required by Remsen's theory;  $(PtCl_6)K_2$ , in the sense of Werner's theory, the two potassium atoms being combined with the  $PtCl_6$  as a whole, or it may be a molecular compound in which two molecules  $KCl$  as wholes combine with  $PtCl_6$  as a whole. The formulas suggested for most minerals are pure guess work. The silicates are usually written as if containing the group  $Si=O$ , by analogy with carbonyl,  $C=O$ , yet there is not a single silicate in which this assumption rests on any experimental evidence, and the little we do actually know of the chemical behavior of silicon speaks against it. Such formulas, if not purely speculative and devoid of all basis and all value, as they frequently are, at best do not represent structure in the sense that the best established organic formulas do; they are at most reaction formulas only, or they represent partial molecules, in the same way that  $CH$  may stand for benzene ( $C_6H_6$ ) or  $HPO_3$  for a metaphosphoric acid. The attempt to interpret the double salts and halides, the compounds with water of crystallization or hydration, the metal-ammonias, the peculiar compounds of the zeolites described by Friedel, and other so-called molecular compounds, in the sense of the valence hypothesis, seems almost hopeless without taking such liberties with it as to render it nearly useless, and without making assumptions of very narrow and limited applicability. One may well question whether this hypothesis must not be very considerably qualified before it can be taken as the basis

of a general theory of the structure of inorganic compounds.

One of the most striking indications of a revival of inorganic chemistry is the recent attempt of Werner to break away from the bonds of the organic-structure theory as applied to inorganic compounds and to establish a more general theory in which valency plays a comparatively insignificant rôle. The arguments on which Werner's hypothesis is founded are too numerous and elaborate to be presented here. Suffice it to say that it was primarily based on that peculiar class of bodies known as the metal-ammonias, consisting of metallic salts, combined with usually six or four molecules of ammonia, and in which the ammonia may be wholly or in part replaced by pyridine, water, acid radicals and other groups. These groups are supposed to be arranged symmetrically about the metallic atom, forming a radical, which, according to its nature, can combine *as a whole* with metals, halogens or other positive or negative groups. Thus, in the compound  $Co(NH_3)_6Cl_3$ , cobalt forms with  $NH_3$  a radical, which combines as a whole with the three chlorine atoms; in  $(PtCl_6)K_2$  the two potassium atoms are combined with the whole group  $PtCl_6$  and not attached to any one part of it; the same applies to  $(NH_4)Cl$ , and to  $K_2(SO_4)$  and  $K_4(FeCN)_6$ . In the formation of these radicals the bivalent  $NH_3$ , the neutral  $H_2O$  and the univalent  $Cl$  can replace each other indiscriminately; the valence theory is, therefore, practically thrown overboard entirely and in place of combination by bonds we have an extension of the old theory of molecular compounds applicable alike to the metal-ammonias, the ordinary oxygen salts, the double halides and the compounds with water of crystallization. It is yet too soon to predict the future of this hypothesis, which has already won numerous active adherents. It is scarcely too much to hope

that it will lead, perhaps with some modifications and extensions, to a more comprehensive theory of structure, and to a clearer definition of the as yet only vague conception of valency. It is the broadest generalization of inorganic chemistry since the discovery of the Periodic Law, and shows that inorganic chemists are no longer willing to be mere imitators and to close their eyes to the existence of whole groups of bodies which do not tally with current theories, and are beginning to see that in these is to be sought the key to a broader inorganic chemistry.

The slow development of inorganic chemistry during the period from 1830 to 1865, as compared with that of organic chemistry, was due, as has been seen, in part to the greater breadth and greater diversity of the field, to the relative absence of leading ideas and leading motives, and to the comparative tractability of carbon compounds as compared with inorganic compounds under the restrictions of the experimental methods in vogue. Prout's hypothesis and allied speculations gave a working hypothesis for a limited number of investigators, but the uncertainty of the atomic weights, which in part was conditioned by the imperfection of analytical methods, prevented any satisfactory results being reached. Absolute purity of materials and absolute accuracy of analytical methods are not of the first importance to the organic chemist, to whom errors of one or two points in the first decimal are seldom of any significance. To the atomic-weight chemist, on the contrary, accuracy is the very first point to be considered; not only must his material be absolutely free from impurities, but his methods must be beyond criticism, and it is only with the increasing perfection of analytical methods, admitting not only of quantitative determinations of the greatest accuracy, but also of the detection of traces of impurities which for ordinary purposes are negligible,

that this kind of work has offered inducements to a large number of workers. The long-wanted, leading idea or motive has been in large part furnished by the Periodic Law. The comparison of the chemical and physical properties of the elements and their compounds, the search for new elements, the fuller investigation of those already known, with the view of more firmly establishing their place in the system, and the redetermination of the atomic weights, are evidence of its influence. Witness, for example, the great activity in the subject of the rare earths, the work on the relative position of nickel and cobalt in the system, and the investigations of the atomic weight of tellurium, having for their object the decision of the question whether this element actually has an atomic weight greater than that of iodine, as the best determinations thus far seem to indicate, or whether it is less, as its chemical analogy to sulphur and selenium requires.

Organic chemistry, with its limited range of temperature, is essentially a chemistry of the beaker, the Liebig condenser and the bomb oven; it demands but comparatively simple and cheap apparatus of glass, not calculated to withstand high temperatures, and as such is within the means of the humblest laboratory. The reverence of the organic chemist for the platinum crucible is something astounding. With improvements in apparatus for producing and materials for resisting high temperatures, new vistas have opened to the inorganic chemist, while the province of the organic chemist, limited as it is by the instability of his compounds, has derived no benefit therefrom. Not only do we owe to this the beautiful investigations of Victor Meyer and others on high-temperature vapor densities, but with the recent development of electrical technology the electric furnace has appeared, and with it a new chemistry, the chemistry of a temperature of 3,500° C. Not only have new

compounds been made which cannot be produced at lower temperatures, but the accessibility of many elements and compounds has been greatly increased. The reductions which Wöhler and Deville effected gram-wise in glass and porcelain tubes can now be carried out in the electric furnace pound-wise and even ton-wise. The manipulation of the current for electrolytic purposes, rendered possible by increased knowledge of the laws of electricity, as well as by ease of its production, is yielding results chiefly in the domain of inorganic chemistry, while the organic chemist is but tardily utilizing the current as a means of oxidation and reduction. Besides the extraordinary development of electro-metallurgy, the preparation of soda and chlorates and other technical processes, the application of electricity to purposes of analysis and for the synthesis of new compounds, such as the rare metal alums, percarbonic and persulphuric acids, and the isolation of fluorine, may be mentioned.

Passing to the opposite extreme of temperature, we find the development of high-temperature chemistry accompanied by the growth of a chemistry of low temperatures. The very recent improvements in the art of producing cold have made liquid air a cheap material, and with its aid Ramsay has been able to fractionally distil liquefied argon and to separate from it the contaminating elements of the same group, neon and xenon, as well as krypton and metargon.

The part played by the spectroscope in chemistry is more or less familiar to everyone. From the further development of the science of spectroscopy it is clear that inorganic chemistry has much to gain. Whether or not the view first suggested by Clarke and long defended by Lockyer be true, that the elements undergo partial decomposition in the stars and nebulae, it is upon this instrument that we must rely for our knowl-

edge of the high-temperature chemistry of these bodies, a chemistry which is wholly inorganic.

The rapid growth of these sciences into which chemistry enters is producing an ever increasing demand upon the chemist for new researches. While the biologist must rely mainly on the organic chemist for his chemical data, no less must the mineralogist and geologist appeal to the inorganic chemist for the solution of many problems in their field. The formation and decomposition of minerals, the disintegration of rocks, the behavior of rock magmas, the phenomena of metamorphism, of ore deposition and vein formation, the influence of high temperatures and pressures—all these afford problems the solution of which is hopeless without the assistance of inorganic chemistry either alone or aided by physical chemistry. The chemist who has to meet the inquiries of the geologist, and who must too often confess our ignorance of the causes of even the simplest phenomena, can not help feeling what a splendid field is here open, awaiting only the advent of workers suitably trained and of laboratories properly equipped for research in chemical geology. The demands of the geologists are unquestionably destined to be among the most potent factors in the revival of inorganic chemistry.

It is not to be expected, nor is it to be desired, that inorganic chemistry will at once sweep organic chemistry from its position of preëminence. The causes to which this is due may outlast our generation, but that the inorganic tide is rising, and that this branch will finally attain its due position, can not be doubted. The recent establishment of a *Zeitschrift für anorganische Chemie*, while it may be deplored as increasing the already too great number of chemical journals, and as tending to widen rather than diminish the gap between the organic and inorganic branches,

is helping to produce a feeling of solidarity among inorganic chemists which never existed hitherto. Even in Germany, the stronghold of organic chemistry, the address of van't Hoff is exciting wide interest, and the *Chemiker Zeitung*, in urging the establishment of independent chairs and laboratories of inorganic chemistry, is advocating what will in time unquestionably be realized.

Inorganic chemistry is fortunate in that its renaissance is coming about at a time when physical methods are in vogue. The prediction of Du Bois-Reymond is being realized; with the aid of physics it is attaining an insight into the dynamical aspect of the science which it could never have reached unassisted. But it is not alone by supplying new methods and suggesting new points of view that physics is aiding the revival of inorganic chemistry. Perhaps equally important is the fact that the rising school of physical chemists, unhampered by the traditions and limitations of organic chemistry, is finding it necessary to explore the whole range of the science in search of material for its investigations. The physical chemist is neither organic nor inorganic, or rather he is either, according to his requirements, but it is precisely because the inorganic field is wider and less developed than the organic that his demands are more likely to be productive of activity.

Energetics is now the basis of chemistry, and it is to be expected, therefore, that inorganic chemistry will not, in the future, have to pass through a period of arrested development and formula worship, such as have so long affected organic chemistry. There will always be compound makers, but their aim will be, not the establishment of constitutional formulas alone, but the study of the laws of chemical energy and the solution of the problem of the nature of matter. We may expect, too, that the still

sharp line of demarcation between inorganic and organic chemistry and between dead and living matter will disappear. The inorganic chemist may not affect the synthesis of a proteid, but he will be able, with his wider knowledge, to contribute more to the solution of the problem of the nature of life than any amount of structurizing and synthesizing alone can do. To comprehend life we must understand carbon, but we can no more fully comprehend carbon without an understanding of the other elements than we can explain the earth without a knowledge of the other planets, or man without a knowledge of the fish. He, then, who pursues inorganic chemistry is not only contributing to a higher development of our science than can be reached by the study of carbon compounds alone, but is perhaps doing as much as the organic chemist toward realizing one of the greatest aims of research, the comprehension of life and its explanation in terms of physical science.

WASHINGTON, D. C.

H. N. STOKES.

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ON THE TOTAL SOLAR ECLIPSE OF  
MAY 28, 1900.

THE next total solar eclipse will be visible as such in places both east and west of the Atlantic Ocean, and it is a matter of some thought to determine where it shall be observed. I have proposed to report to the governing board of Williams College that it is practicable to observe it on both sides at points to be fully determined later, as at present there is rather more than a year's time to make the needful arrangements.

The two countries where it shall be observed seem to be Portugal and our own Southern States, in the neighborhood of Coimbra and that of Norfolk, in Virginia, or perhaps farther south. The only doubt is the more or less uncertainty of weather. That, however, cannot be avoided, as the meteorologists are not yet able to predict with much certainty or at all for more