The Study of the Atom; or, The Foundations of Chemistry.

THE STUDY OF THE ATOM;

OR,

THE FOUNDATIONS OF CHEMISTRY.

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INTRODUCTION.

The purpose of this work is to trace the atomic theory of chemistry from its earliest conception to the present day. This forms the foundation of all chemical theory and has been offered as the best explanation of the constitution of matter and of the universe. This theory has had a longer life than any other philosophical or scientific conception, and has to-day more nearly its ancient form. It has lived through bitter attack, dialectic strife, and even persecution, and can number its martyrs. It has called to its service the master minds of the world and the greatest ingenuity in experiment and in logic. It is not to be presumed that such a conception can be dismissed in a few slighting sentences or overturned by one or two crude hypotheses.

It is no part of the plan of this book to study all branches of chemical theory. Only such will be taken up as bear directly upon the question of the constitution of matter. It will be found, however, that this includes most of the important theories.

Where a great science is founded upon a theory, in so far as the explanation of its facts are concerned, it is fitting for those who love that science, and higher still, love truth, to examine well its foundation, to trace it back to its far-off inception and to test it by all wise and skilful methods for finding out the truth, feeling assured that only good can come from such examination. It will strengthen them to know how sure is their foundation, or if it be found unstable, it will be wise to discard it before more harm is done. For the false can not lead up to truth and it is toward truth and truth alone that the labors of all students of Nature should tend.

CHAPTER I.

Ancient Views as to the Nature of Matter.

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ANCIENT VIEWS AS TO THE NATURE OF MATTER.

The Constitution of Matter. A theory as to the constitution of matter is an effort at making clear the conditions upon which rest the filling of space with distinguishable entities and the change of these. The history of such theories is closely connected with the development of all science, for its object embraces the entire content of all experience.[1] From the very earliest time man has taken a strong theoretical interest in the material world and developed from a metaphysical standpoint his views as to the world formation.[2] That this theoretical interest preceded, however, that practical interest in nature which led to its subjugation so as to supply immediate necessities can scarcely be maintained. The technical man preceded the philosopher, the needs of daily life were first supplied.

Theory and Empiricism. The theories of chemistry take their rise in the cosmogonies of the philosophers or their efforts at accounting for the origin and building of the universe. Experimental chemistry, on the other hand, was at first eminently practical and was derived from the empirical knowledge of the metal worker, the potter, the cook and the dyer. It is to be expected then that the technical man should altogether disregard the theories of the metaphysician as to the world around him, or that he should use only so much of these theories as come well within his experience. Thus the corpuscular theory of the

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[1] Lasswitz: "Geschichte der Atomlehre," 1, 1.

[2] Lasswitz, 1, 6.

mechanician, Hero of Alexandria, and of the physician, Asclepiades of Bithynia, stood in close relation to the atomic theory of Democritus, and yet was not that theory.

Purpose of the Book.

It is the purpose of this book to trace the rise and development of one of these theories which sprung from the early cosmogonies—its inception by the meta-physician and its tardy acceptation by the man of experiments after he had satisfied himself that it agreed with his experience and afforded the most satisfactory explanation of that experience. This theory has been known for some twenty-four hundred years as the atomic theory. The field includes, then, man's study of the atoms, speculative and experimental, from the dawn of science to the present day.

The Two Theories.

Without going into a detailed development of them at present, it may be stated that there are two possible theories as to matter. One is that matter is infinitely divisible and that no limit can be placed to the possibility of its subdivision. The other is that matter is not infinitely divisible, but that eventually particles will be reached which are no further divisible by any known means. Such particles were called atoms by the Greek philosophers and this theory became known as the atomic theory.

Chinese Theories.

Probably the most ancient document extant containing reference to this idea is the Shoo King,[1] which is one of the oldest and most esteemed of Chinese classics, and here the idea is rather that of elementary particles than of atoms. This treatise is an historical work and comprises a document of

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[1] Cited by Gladstone in Address to Chemical Section, British Association, 1883. *Chem. News*, **48**, 151 (1883).

still greater antiquity called "The Great Plan with Its Nine Divisions." This purports to have been "given by Heaven to the Great Yu to teach him his royal duty and the proper virtues of the various relations." Of course there is no perfect agreement as to the date of this document and the opinions vary widely concerning it, but it seems fairly safe to assign it to a time more ancient than the writings of Solomon. The first division of the Great Plan relates to the five elements. The first element is named water; the second fire; the third wood; the fourth metal; the fifth earth.

Hindoo Theories.

Without attempting to settle the question of priority in this conception of primal elements it is sufficient to state that a similar idea is found in the early literature of several nations, notably among the Indian races, though the number and names of the elements may differ.

In the Institutes of Menu the subtle ether is spoken of as being the first created. From this, by transmutation, came air and this through some change became light or fire, and by a further change in this came water from which lastly earth is deposited. This was the accepted philosophy of the Hindoos and Buddhists. It extended over Asia and found its way into Europe. It has been claimed that it was elaborated in the philosophy of the Greeks.[1]

These early ideas as to primal elements would seem to have little or no bearing upon the theory of atoms. In thinking of the genesis of matter, however, the first thought was as to the primal element or elements and the conception of the atom was most probably evolved from this idea.

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[1] Gladstone: *Loc. cit.*

Atomic Theory of Kanada.

It is exceedingly difficult to interpret aright many of the obscure, ancient writings of China and India. Yet in these literatures definite traces of the theory of atoms can be distinguished. Thus an atomic theory has been proposed by Kanada, the founder of the Nyaya system of philosophy, of which this theory forms a distinguishing feature.[1] First as to the elements it is stated by Kapila, founder of the Samkhya philosophy, that there are five subtle particles, rudiments or atoms, perceptible to beings of a superior order but unapprehended by the grosser senses of mankind, derived from the conscious principle and themselves productive of the five grosser elements, earth, water, fire, air and space.

Kanada considered material substances to be primarily atoms, secondarily aggregate. He maintains the eternity of atoms.

"The mote which is seen in a sunbeam is the smallest perceptible quantity; being a substance and an effect, it must be composed of what is less than itself. This again must be composed of what is smaller, and that smaller thing is an atom. It is simple and uncomposed else the series would be endless; and were it pursued indefinitely there would be no difference of magnitude between a mustard seed and a mountain, each alike containing an infinity of particles. The ultimate atom then is simple.

"The first compound then consists of two atoms, the next consists of three double atoms. Two earthly atoms concurring by an unseen virtue, creative will of God, or other competent cause, constitute a double atom of earth and by concourse of three binary atoms a tertiary atom is produced. The atom is reckoned to be the sixth part of a

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[1] "History of Hindu Chemistry," Ray, 5, 6.

mote visible in a sunbeam. The atoms are eternal, the aggregates are not. The aggregates may be organized organs and inorganic." No definite date can be assigned to Kanada but he seems to have lived before the time of Democritus.

Mathematical Derivation of the Theories.

According to another view the two theories as to the constitution of matter have been derived from mathematical considerations as to number, time and space, and not deduced from theories as to the genesis of matter. This is ingeniously worked out as follows :[1]

It is probable that the first exact notions of quantity were founded on the consideration of number. It is by the help of numbers that concrete quantities are practically measured and calculated. Now number is discontinuous. We pass from one number to the next *per saltum*. The magnitudes, on the other hand, which we meet with in geometry are essentially continuous. The attempt to apply numerical methods to geometrical quantities led to the doctrine of incommensurables and to that of the infinite divisibility of space. Meanwhile the same considerations had been applied to time so that in the days of Zeno of Elea time was still regarded as made up of a finite number of "moments," while space was confessed to be divisible without limit.

Aristotle pointed out that time is divisible without limit in precisely the same sense that space is. It was easy to attempt to apply similar arguments to matter. If matter is extended and fills space the same mental operation by which we recognize the divisibility of space may be applied, in imagination at least, to the matter which

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[1] Clerk-Maxwell, article on "Atoms" in Encyc. Brit.

occupies space. From this point of view the atomic doctrine might be regarded as a relic of the old numerical way of conceiving magnitude and the opposite doctrine of the infinite divisibility of matter might appear for the time the most scientific. The atomists, on the other hand, asserted very strongly the distinction between matter and space. The atoms, they said, do not fill up the universe. There are void spaces between them. If it were not so, Lucretius tells us, there could be no motion, for the atom which gave way must have some empty space to move into. It would be better, however, to postpone an account of the arguments along this line until the views of the early Greek philosophers have been studied.

Greek Theories.

By far the fullest and clearest theories have come to us from the Greeks. How far these originated with them it is difficult to say and the point has been vigorously discussed without reaching any satisfactory conclusion. Gladisch[1] sees in the Pythagorean theories the philosophy of the Chinese; that of the Hindoos in the Eleatics; that of the Persians in Heraclitus (Lasalle maintains that Heraclitus derived his philosophy from India); that of the Egyptians in Empedocles and that of the Jews in Anaxagoras. The truth would rather seem to be that there were racial ideas held in common. The Greeks, coming from Asia as did the other Indo-Germanic races, brought these theories with them, modified them according to their own peculiar conditions and environment and developed them by their own powers. Burnet regards the idea of the introduction of Eastern philosophy into Greece as fanciful and probably a suggestion of Egyptian priests and

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[1] Zeller: "Pre-Socratic Phil.," I, 35.

Alexandrian Jews.[1] Indian Science, it has been claimed, came from Greece in the train of Alexander's army.

It is not altogether easy to form a correct idea as to the theories of the earliest of the Greek philosophers since we are largely dependent upon the record and interpretation of them given in the writings of later followers, antagonists, or lexicographers. In the case of many of them only scattered fragments of their writings have been preserved. We will consider the views of these philosophers in detail.

Ionic School.

The earliest Greek cosmogonists were those of the Ionic school. These men were characterized by their love of knowledge and their diligent search for it everywhere. They were not satisfied with the mere observation of phenomena but sought for law in everything and strove to construct systems of the universe. To find out the genesis of all things was a fascinating thought to them. In the midst of the changes surrounding them, especially those of generation and decay, they sought for something primeval and unchanging. Burnet has pointed out[2] that their word *φὕσις*, from which our word physics comes, was used by the early cosmogonists to express the idea of a permanent and primary substance so that *περὶ φυσέως* does not mean, as ordinarily translated, "On the Nature of Things" but "Concerning the Primary Substance." There are traces of a careful and minute investigation of nature by these philosophers in search of evidence to support their theories. Thus Xenophanes, to substantiate certain of his views, made a careful investigation of the fossils and petrifactions in such widely separated localities as Paros, Malta and Syracuse.

[1] Burnet: "Early Greek Phil.," 15.

[2] Burnet: "Early Greek Phil.," 10.

Thales of Miletus, 600 B. C.

The founder of the Ionic school was Thales of Miletus who lived about 600 B. C. He left no writings and we are dependent upon Aristotle for our knowledge of his views. These he gives in three statements: (1) The earth floats on water; (2) Water is the material cause of all things; (3) All things are full of gods, and the magnet is alive, for it has the power of moving iron. His view of the universe would seem to be a space filled with a fluid, water, and out of this principle the solid earth and all things upon it were formed. These he endowed with life, and following him all the Ionic philosophers were hylozoists. He was ignorant of the atmosphere or air, the ἄηρ of Homer meaning first the mist or vapor such as that rising from the ocean.

Anaximander, 546 B. C.

Nearly all that is known of the next of these philosophers, Anaximander (also of Miletus, 546 B. C.), is from the account given by Theophrastus. According to him, Anaximander maintained that neither water nor any similar substance was the primal element but a substance differing from any of them and merely described as infinite. Into that from which things took their rise they passed away once more. The origin of things was not due to any alteration in matter but to the separation of "opposites from the boundless substratum." There was an eternal motion in the course of which was brought about the origin of worlds. His theory then was one of the Boundless or Infinite, one eternal, indestructible substance. He saw no up nor down in nature.

Anaximenes.

Anaximenes, who is spoken of as an associate of Anaximander, said also that the substratum was one and infinite. He did not, however, consider it indeterminate in character but called it air, meaning by this, probably, vapor or mist. It is always in motion and differs in different substances in virtue of rarefaction and condensation. The introduction of the idea of rarefaction and condensation constitutes a distinct advance as, where everything is formed by the transformation of one substance, all differences must be purely quantitative. The previous theories are incomplete and impossible unless diversities are considered as due to the presence of more or less of the *materia prima* in a given space.

Pythagorean School.

The philosophy of Pythagoras and the Pythagorean school was of a religious and political character rather than physical. It is also largely mathematical and distinct from the theories of the early cosmogonists. Little is known with certainty as to Pythagoras himself and his beliefs, but the views of the school founded by him have in them the germ of some later theories of science. The distinctive feature of the Pythagorean school was, that number is the essence of all things and everything in its essence is number.[1] Numbers are not merely qualities of things but the substance of things. While numbers are regarded by us only as the expression of the relation of substance they thought that they found in them the substance or the real. All numbers are divided into the odd and even and to these the third class, the even-odd (*ἀρτιοπερίσσον*) was added. Everything united in itself opposite characteristics, the odd and even, the limited and unlimited. The primary constituents of a thing, therefore, are dissimilar and opposite in character. The uniting bond is harmony.[2]

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[1] Aristotle's, Metaphys. I, 5.

[2] Philolaus Ap. Stob., I, 460.

According to Eudorus[1] the Pythagoreans reduced all things ultimately to the one, or unity. This is the first principle, the efficient cause of all things. Duality is passive matter. Unity, or perfection, as opposed to duality, or imperfection was called the monad. It is quite difficult to decide whether the Pythagoreans regarded their numbers as something corporeal, or bodies as something immaterial. Still, whether from a false interpretation or not, their theory has come to be regarded as the theory of the harmony of nature, its essential oneness and the derivation of all things from one, a sublime thought in itself and one which has played a large part in the philosophy of the past centuries and again comes into prominence in the speculations of the present day.

Anaxagoras, 500 B. C.

Anaxagoras, of Klazomene, is one of the first of the philosophers whose views approximated to an atomic theory. Others who had preceded him had advanced theories as to the primal elements but not as to the internal constitution of matter. According to the theory of Anaxagoras there was first a chaos. All matter was in the form of mingled particles in infinite disorder. These particles were called by Aristotle in later times homoeomerous (*ομοιομερείαι*) which means "like parts." That is, these very small particles were similar to the masses of matter afterwards formed by their aggregation. They were rather molecules than atoms. The *νο̃υς*, or designing intelligence, brought these out of chaos and formed of them matter as known to us. Anaxagoras' statement that there is a portion of everything in each particle is best explained as meaning that in each was to be found a portion of the qualities moist and dry, hot and cold, light and dark, but

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[1] Simpl. Phys., 39. A.

the predominating portion determined the character of the particles. Among these particles the *νõυς* began a rotary motion through which the like particles were gradually brought together and separated out in the form of the various known substances. As Rodwell says, this vertical motion was supposed to have drawn together the similar homoeomerous by a process something like that of gathering the gold grains in a pan during the process of washing.[1] In other words, this acted very much as water does in sorting out substances of different specific gravities. According to Anaxagoras then, on dividing a body, as a grain of earth, particles of earth are obtained. This can be continued indefinitely and still the grains resemble the original grain of earth. There is, therefore, no limit to such subdivision. This became later the philosophy of the Peripatetics or Pythagoreans. Such particles are manifestly not atoms which were not necessarily like the mass and were indivisible. To Anaxagoras bone was made up of minute particles of bone, blood of minute drops of blood, water of minute drops of water. This would necessitate the original existence of a distinct particle for every distinct kind of matter.

His introduction of an external cause to produce the motion is noteworthy, but too much stress must not be placed upon this mind or designing intelligence or disappointment such as that felt by Socrates or Aristotle may follow.[2] Aristotle, says Anaxagoras, used mind as a *deus ex machina* to account for the formation of the world and whenever he is at a loss to explain anything, he drags it in. But in other cases he makes anything rather than mind the cause.[3]

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[1] Rodwell: "Birth of Chemistry," 18.

[2] Plato: Phaid, 97 B.

[3] Aristotle's Metaphys. A. 4 985a.

Heraclitus, 500 B. C.

According to Heraclitus, the next one of these philosophers, all things are one. "It is wise for those who hear, not me but the universal reason, to confess that all things are one."[1] He assumed as the primal element, fire. In his opinion there was nothing fixed and permanent in the world but all was involved in constant change as the waves of a river are constantly replaced by those following.[2] The restless alteration of phenomena became comprehensible to him by considering the world a fire. Fire was the life of nature. Everything was created by fire and was dissolved into fire. Fire was not an unvarying substance out of which all things were formed while it itself remained unchanged qualitatively like the elements of Empedocles. On the contrary it was the essence which passes ceaselessly into all elements, the universal nourishing matter which, in its eternal circulation, permeates all parts of the cosmos, assumes in each a different constitution, produces individual existence and again resolves itself and by its absolute motion causes the restless beating of the pulse of nature.[3] The elements of the physicist were those which amid the change of particular things remained unchangeable. To Heraclitus, fire was that which by constant transmutation caused the change. The harmony of the world was due to the strife of opposites.

Empedocles, 500 B. C.

Empedocles sought a middle course between Heraclitus who said that matter was always changing and Parmenides who denied change, motion, generation, and decay. Qualitative change in the original substance was to him

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[1] Patrick: "Fragments of Heraclitus," I.

[2] Patrick: "Fragments of Heraclitus," XLI.

[3] Zeller: "Pre-Socratic Phil.," II, 23.

unthinkable but there is change for particular things, and the conditions of the world are subject to perpetual change. These phenomena of change he reduced to a movement in space, to the combination and separation of the underived, imperishable and quantitatively unchangeable substances. In this he is the first to clearly define the elemental constituents or elementary bodies. He had to assume several of these in order to explain the multiplicity of things. Aristotle states[1] that Empedocles was the first to admit the four elements—earth, air, fire, and water, a theory which he himself adopted and which was generally accepted for centuries. This theory, however, in a very similar form was common to several races long before the time of Empedocles. Further, in his system, the constancy of matter was maintained and all vacuum denied. He did not speak of a single substratum of all the elements. They were distinctly underived. Nor did he speak of ultimate atoms. The fact that his elements were unchanging may be regarded as the most important advance in thought leading up to the unchanging atom. The dualistic idea as to force or controlling and directing influences is to be seen in the "Opposites" of Anaximander, the strife of the opposites bringing about harmony according to the system of Heraclitus (who gives as instances the high and low notes of music and the contrasted colors of the painter) and in the Light and Darkness of Parmenides. It is still more clearly brought out in the love and strife of Empedocles. In his system the contending forces cause the combination and separation of the elements. There were four cycles or spheres. In the first, all the elements are mixed by love; in the second, love is passing out and strife coming in (partial

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[1] Aristotle's Metaphys. I, 4. 985 a 31.

separation and partial combination); in the third, love is banished and there is complete separation; in the fourth, love is gradually bringing the elements together again and strife is passing away. Such a world as ours can exist in only the second or fourth cycles.

Leucippus, 500 B. C.

Leucippus is regarded as the founder of the Atomistic school. While the date and place of his birth are not recorded it is known that he lived in the middle or latter part of the fifth century B. C. and that he was the contemporary of Anaxagoras, of Klazomene, and Empedocles, of Agrigentum. His most famous pupil was Democritus who later became his associate and developed his philosophy. No writings of his are known and in the light of the greater fame of his pupil, Democritus, he was ignored by both Epicurus and Lucretius. He is referred to by Aristotle.

According to Leucippus all things consisted of empty spaces and atoms (*ἄτομος*, from *α* and *τέμνειν*, to cut), space being infinite in magnitude and atoms infinite in number. These atoms were further indivisible, having only quantitative differences between one another and being always in motion. Instead of the *νοῦς* or designing intelligence of Anaxagoras, *ἀνάγκη*, or necessity, was the promoting cause of all things. Worlds are formed by the falling together of atoms, varying in shape and weight, in empty space, their impact giving rise to a new eddying motion and the motion causing the formation of all substances. These atoms were quite distinct from the homoeomerous of Anaxagoras, as they were not necessarily similar to the substances formed from them but were the "seeds of things".

Eleatic School.

It is mainly through fragmentary quotations and the statements of Aristotle that the works of the Eleatic philosophers are known to us. The most prominent of these philosophers are Xenophanes, Zeno and Parmenides. This philosophy was monotheistic, believing in one underived all-embracing being. Change was regarded as impossible in a universal sense and they were opposed to the idea of multiplicity and plurality. The atomists were classed with or included in the Eleatic school and Aristotle remarks upon the affinity existing between the two.[1] But they differed greatly as to motion and change, the possibility of either being denied by the Eleatics. Zeno's arguments against the possibility of motion will be introduced later as a specimen of their dialectics. While the eternal oneness of nature was maintained, the Eleatics proper did nothing to advance the doctrine of atoms.

Democritus, 460 B. C.

The theory of Leucippus was taken up by Democritus, of Abdera, who had been his pupil and then his associate but who excelled his master as a deep and orderly thinker. He defended and developed the theory of atoms to such an extent that to him is usually accredited the title of founder of the Atomistic school. "The existence of atoms must be admitted," he said, "because of the principle that nothing is made of nothing." "If every substance is divisible to infinity and the division is never arrested, we come to one of two things: either nothing remains or something is always left. In the first case the body was made up of nothing or it was composed of an apparent reality. In the second case, one might ask, what is it that remains, an entity or a space? But then the

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[1] Aristotle: "Gen. et Corr.," 1, 8.

division could not have been exhausted. Does a point remain? But whatever may be the number of points which are suggested, it will never fill a space. Therefore it is necessary to admit the existence of real indivisible elements.''[1] This line of reasoning was borrowed from or very similar to that of Zeno.[2] Further, Democritus reasoned that the atoms varied not only in size and in weight but the main distinction between them was in shape.[3] The smallest atoms are at the same time the lightest. The atoms are absolutely simple and homogeneous, differing in this from those of Anaxagoras, and are impenetrable: two atoms cannot occupy the same space at the same time. Each atom resists the atom which tends to displace it. This resistance gives an oscillatory motion which is communicated to neighboring atoms which transmit it to the more distant atoms. From this springs a gyratory motion, a rotation which is a type of all the motions in the world.[4] The Eleatics had formed the concept that being can only be defined as indivisible unity. Leucippus and Democritus supposed the corporeal to be composed of parts incapable of further division; all consists of atoms and the void. All the properties ascribed by the Eleatics to being are transferred to the atoms.[5] These atoms are too small to be perceived by the senses since every substance perceptible to sense is changeable and divisible.

Little is known as to Democritus' opinion about the four elements of Empedocles. Fire alone seems to have had for him any very great importance among the theories of primal elements. He considered fire the moving,

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[1] Aristotle: "Gen. et. Cor.," I, e, 2, 8.

[2] Simplicius Phys. 30,a.

[3] Aristotle, Phys. I., a.

[4] Plutarch: "de Placit philos.," I., 26; Stobae: "Eclog. phys.," I., 394.

[5] Zeller: "Pre-Socratic Phil.," II., 219.

living principle throughout nature. On account of its mobility he supposed it to consist of round and small atoms. In the other elements there is a mixture of heterogeneous atoms and they are distinguished from one another only by the magnitude of their parts.[1] The atoms are in ceaseless movement,[2] which was so necessitated by the nature of things that he considered it to be without beginning.[3] This movement was a result of their weight. The movement of all atoms would be in the same direction. The inequalities in size and weight bring about unequal velocities. They impinge upon one another and the lighter are forced upward by the heavier. From the resultant of these two motions, the concussion and recoil of the atoms, there arises a circular or whirling movement. From this circular motion the universe was derived. Through this movement of the atoms, homogeneous particles are brought together, being alike in weight and form, and so sink into the same place.[4] From the combination of atoms, compound bodies are formed. The atoms he thought to be infinite in number and infinitely various in form and size. Democritus and the atomists endeavored to give a strictly physical and material explanation of nature. Nothing happened by chance ; all could be referred to natural causes. Democritus has been spoken of as an empiricist rather than a philosopher. Certainly he devoted more attention to the explanation of natural phenomena than any of his predecessors and quite possibly he accumulated more empirical material than he was able to master with his scientific theory. He did not neglect experimental science and sought in actual knowledge of things a basis for his theories. His system

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[1] Zeller: "Pre-Socratic Phil." II., 234.

[2] Aristotle's "Metaphys.," XII., 1070.

[3] Cicero, Fi, I., 6, 7.

[4] Sextus: Math. VII., 116.

is throughout materialistic, dispensing with all save corporeal being and all force save gravity.

Plato, 427 B. C.

Plato, in his teachings as to world formation, deemed it necessary to assume the existence of the four elements of Empedocles. In his physical derivation of these he makes use of the theory of Philolaus, assigning geometrical forms to the elements from considerations, as he says, of their mobility, magnitude, weight, penetrating power, etc. The fundamental form assigned to fire is the tetrahedron (Democritus considered the fire atoms spherical because of their mobility); of air, the octahedron; of water, the icosahedron; of earth, the cube.[1]

All superficies, he says,[2] consist of triangles and all triangles arise out of the two different right-angled triangles, the isosceles and the scalene. Out of six scalene triangles arises an equilateral triangle and out of four isosceles triangles arises the square; out of the square is formed the cube; out of equilateral triangles the three remaining bodies. From this it may be seen that his groundwork was space and the atoms, not matter filling space but certain parts of space mathematically limited and comprehended in definite figures.[3]

The properties, combinations, decompositions and other changes of these elements Plato discusses at length. His theory is really one of the continuity of matter which being space itself fills all space. But he overlooked or disregarded certain difficulties pointed out by subsequent philosophers. For instance,[4] the four elementary forms chosen by him can never fill up any space so as to leave

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[1] Plato 55, D.

[2] Plato 53, C.

[3] Zeller: "Plato and the older Academy," 374.

[4] Aristotle: "de Coelo," III. 8.

no intermediate space, nor can a sphere (the supposed form of space) ever be entirely filled by rectilinear figures, and lastly the dissociation of an element into the triangles of which it was composed must produce a void as there was nothing between these triangles.

Heracleides. The only Platonist whose views are novel enough to make them suitable for citation here is Heracleides. While he may be considered a follower of Plato, he made some noteworthy divergences from his doctrine. He assumed as the primary constituents of all things minute bodies, themselves not compound nor made out of anything else. These atoms differed from those of Democritus in that they were supposed to be capable of affecting or influencing one another. This was not a mechanical influence, but one of actual interdependence.

Aristotle, 384 B. C. The most famous of Greek philosophers and the one who exercised the greatest influence upon subsequent thought was Aristotle. In his eighteenth year he entered the school of Plato, at Athens, and continued in it until the death of the master, twenty years later. The effect of this could not fail to be great upon the philosophic system of Aristotle, although he saw the weak points of his teacher and in after years criticized them unsparingly. His own followers became known as the Peripatetics.

Aristotle did not believe in a vacuum or void. He had defined space as the limit of the surrounding body in respect to that which it surrounds.[1] There is then, no space where there is no body as empty space would be an enclosure enclosing nothing. This was, of course, directly contrary to the teachings of the atomists. He further

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[1] Aristotle : "de Coelo," IV., 3, 310, 6, 7.

differed from the atomists in asserting that there was a qualitative distinction between sorts of matter, a qualitative alteration of material, and that there might be such a combination of materials as to cause the change of their qualities.

Aristotle opposed the idea of infinitely small bodies. He pointed out conclusively the fallacies of the Platonic system. How, for instance, can surfaces which have no weight unite to form bodies which have? He could not regard it as proved by Democritus that everything could be deduced from a primal homogeneous matter.

It is interesting to see how Aristotle derives his most conclusive argument against the homogeneity of matter from the phenomenon of gravity. Democritus, like Aristotle, was ignorant that all bodies mutually attract each other, that within the terrestrial influence they all gravitate towards the center of the earth, that the inequality of the rate of their descent is caused by the resistance of the air, and that the pressure of the atmosphere causes the ascent of fire (heated gases), vapors, etc. We have become so accustomed to the traditional and conventional views of nature that it is difficult for us to comprehend the point of view of these earlier philosophers or to see the puzzling questions which surrounded them. Democritus believed that all the atoms fall downward in the void, but that the greater fall more quickly than the less, deducing from this hypothesis the concussion of the atoms and the pressure by which the lesser are driven upwards. For the same reason he held that the weight of composite bodies, supposing their circumference equal, corresponds to their magnitude after subtraction of the empty interstices. Aristotle demonstrates that this hypothesis is false: there is no above nor beneath in infinite space, and consequently no natural tendency downwards; all bodies must fall with equal rapidity in a void, nor can the void within bodies make them lighter than they really are. But Aristotle goes farther and, ignorant of the actual phenomena which have to be explained, rejects altogether Democritus' theory of empty space, a theory which could not be verified by the factors known to ancient science but the foremost feature in the speculative theory of Democritus. He looked upon the fact that certain bodies always tend upwards, rising more quickly with increasing bulk, as a phenomenon quite inexplicable on the hypothesis of absolute homogeneity of matter. For, if all bodies were composed of the same matter, all would be heavy and nothing light in itself. Although it may be that of two bodies of equal size, the denser might be the heavier, nevertheless a great mass of air or fire would necessarily be heavier than a small quantity of earth or water, a view which he regarded as impossible. If gravity be determined by bulk, then a great mass of rarer material would be heavier than a small one of denser and accordingly would move downwards. If, on the contrary, it is said that the more vacuum a body contains the lighter it is, it may be answered that a great mass of denser and heavier substance includes more vacuum than a small one of the rarer sort. Finally, if the weight of every body corresponded to the proportion between its bulk and the empty interstices, a great lump of gold or lead might sink no faster than the smallest quantity of the same stuff.

He concludes that we are driven to assume the existence of bodies heavy or light in themselves, which move respectively toward the center or circumference of the world; and this is possible only when we conceive them as differing qualitatively and not merely by the figure or magnitude of the elementary ingredients.[1]

Not only, in his opinion, did the materials of the world differ qualitatively, but they were subject to qualitative transformations. Unless this was admitted, the apparent transmutation of matter must be explained by a simple expulsion of existing materials (Empedocles and the atomists) or by a change in the figures of the elements (Plato). The change of water into steam was, in the theory of Aristotle, a transmutation of the elements, a qualitative change of material. Otherwise he could not explain the great change of bulk if the steam had previously existed in the water without change or difference. This formation of steam from water was a difficult problem to the atomists and could not possibly be explained by them on the ground of increased repulsion of the atoms or their lessened cohesion as in the modern theory because the atoms of Democritus were incapable of any internal change. Empedocles and Anaxagoras explained steam as a kind of air emanating from water, and the atomists looked upon it as a complex of atoms escaping from water in which they had been previously imprisoned. Of course, this theory would leave an untransformed remnant which did not accord with experience. Aristotle then rejected the existence of the indivisible and of voids. He did not regard a combination (*σύνθεσις*) of bodies as an absorption of one sort of matter into another, nor a merely mechanical union or junction as the atomists did. When two materials then combine, neither of them remains the same; they are not merely blended in invisible minute particles but both have passed wholly into a new material wherein they re-

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[1] Zeller: "Aristotle and the Earlier Peripatetics," I, 447, et seq.

main potentially inasmuch as they can be again extracted from it.[1]

Epicurus, 342 B. C.

Epicurus founded one of the most distinctive and lasting of the Greek schools of philosophy. He received instruction in the system of Democritus and Plato and was acquainted with the writings of the chief philosophers who had preceded him. From these he borrowed important parts of his doctrines, but his debt to Democritus was by far the largest. While he wrote many treatises, only a few fragments have been saved. He was peculiarly fortunate, however, in having a disciple, T. Lucretius Carus, who, some 250 years after his death, with far more facile pen than the master and more pleasing style, recorded and defended his system and transmitted it to posterity. In his great poem, *De Natura Rerum*, Lucretius has carefully reproduced the Epicurean beliefs as to natural science.

It is, of course, beyond the purpose here to discuss this system of philosophy in any other regard save as it touches upon natural science. It is sufficient to say that it was thoroughly materialistic, endeavoring in mechanical cause to find the explanation of all things. Nor is it necessary to repeat those atomistic portions of the system which were borrowed from Democritus. Bodily reality was for him the only form of reality. Corporeal substance was the only kind of substance. Besides this, the assumption of empty space was necessary to explain phenomena. All bodies of which we are sensible are made up of parts. If they could be divided infinitely, they would ultimately be resolved into the non-existent. The indivisible ultimate components are the primary

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[1] Aristotle: "Gen. et Cor.," I, 10; 327 b 22; 328 a 10.

bodies which, differing in size, shape, and weight, have no empty spaces in themselves. They are too small to impress themselves upon the senses, still they are not mathematical points.[1] All material things are composed of these atoms and voids or empty spaces. Epicurus endeavored to meet the objection of Aristotle to the theory of the downward motion of atoms, namely, there could be no up and down in space, by appealing to experience, something always appearing above our heads and others beneath our feet.[2]

His most important deviation from Democritus was in his denying that the perpendicular fall of the atoms could bring about a meeting and so cause the rotary motion held by the latter as essential for world building. According to Epicurus, all atoms would fall equally fast in empty space, and a meeting to produce the rotary motion would be impossible if they fell perpendicularly,[3] a bit of reasoning borrowed from Aristotle. It was necessary to assume a slight swerving aside from the perpendicular in falling, to bring about such a meeting. And this was further a necessary assumption in order to account for freedom of the will in animals.

Again,

If all motion in a chain were bound
If new from old in fixed order flowed,
Cause linked to cause in an eternal round.
If atoms no concealed clinamen had,
Cause to create and break the bond of fate,
How could free will in animals exist?[4]

This declination (clinamen) from the straight line sprang from the self motion of the atoms. Thus meeting

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[1] Lucretius, I, 266.
[2] Diogenes Laertius, 60.
[3] Lucretius: "De Natura Rerum," II, 225.
[4] Lucretius: Book II, 251.

became possible and so all the sequences of re-bounding, rotary motion, clustering of atoms and world-building.

This atomic declination is the most original part of the philosophy of Epicurus and is spoken of as "the central and truly original point of the Epicurean system."[1] It was necessary as his reasoning brought him to the dilemma of choice between the creative design of the older philosophers and the fate or necessity of the Stoics, neither of which satisfied him. This theory gives to the atom of the senseless stone the same self-motion or spontaneity or will that was supposed to exist in the atoms of the human body, and not merely does this reside in the individual atom but in the mass of stone.[2] It is not to be understood, however, that Epicurus endowed his atoms with life. It was with will only, and it is difficult to decide whether Epicurus limited this declination to the origin in the case of inanimate matter and continued it in force for all endowed with life and equally difficult to see how he reconciled it with the idea of unchanging atoms and fixed, constant law or necessity, a principle very strongly insisted upon by him and his followers.[3]

Summary. Thus two distinct schools of thought were founded among the Greek philosophers. The Peripatetics, followers of Aristotle, looked upon matter as continuous and filling all space, and denied the existence of indivisible particles or void spaces. On the other hand, the Epicureans, or atomists, adopted the theories of Democritus as modified by Epicurus and maintained that matter does not fill all space and is not infinitely divisible but that it is built up of atoms or particles which cannot be further divided. It was not possible for a final de-

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[1] Guyan: "La Morale d'Epicure," 2nd ed., p. 99, note.

[2] Masson: "Atomic Theory of Lucretius," 219.

[3] Masson: "Atomic Theory of Lucretius," 221.

cision to be reached between these two views since all direct proof was lacking. These intellectual giants had reached the limits to which it was possible for the observations and appliances at their command to lead them. No one can thoughtfully study the works of these philosophers without paying tribute to the intellectual acumen and the masterly logic which enabled them to reason so clearly upon matters so difficult to comprehend as the primal elements and the nature of all things. Especially is admiration aroused when one considers the imperfections of their actual knowledge and the almost total absence of means for increasing knowledge and correcting erroneous observations.

The Greeks as Observers.

It may be questioned whether the Greeks were a race possessing the qualities of mind necessary for great advance in practical science, which comes only through patient drudgery, the slow amassing of observations, and painstaking accuracy as to details. Yet their unequaled masterpieces of sculpture and fidelity to the details of anatomy would indicate the possession of great powers of observation, of imitation, and of perfection of mechanical skill.

The Greek philosopher possessed, however, only the crudest methods of observation, not to be compared with the wealth of means at the service of the modern man of science. He had the very difficult task of constructing the beliefs and defining the elementary physical conception when the unaided eye determined the limit of the research and the empirical processes were few and unreliable. His rule and compasses and a few makeshifts constituted his stock of apparatus. It would have been miraculous if he had not made mistakes, it was almost a miracle, certainly a great triumph of reason, that he saw as far and as clearly as he did.

In the matter of observation and classification the Greeks seem to have reached a high plane of excellence. Taking Aristotle as the highest type, we find in his Natural History such careful observation of species and variations of habits of animals that his work can serve as a foundation in zoological researches of the present day, and although in his division of animals into the blooded and bloodless he made use of a faulty generalization, his accurate observation of resemblances and differences enabled him to separate properly the great classes of vertebrates and invertebrates. The estimate of Aristotle given by Tyndall[1] is probably a fair picture of the failings of the Greek philosophers as men of science. He finds in his ideas indefiniteness, a confused understanding, too great reliance upon the use of language which leads to the self-deception that he was the master of a great subject when he had not even succeeded in grasping the elements of it. He put words in the place of things, subject in the place of object. He preached induction without practicing it in that he reversed the proper order of research by proceeding from the general to the special instead of from the special to the general.

The Greeks seem to have made little true use of inductive logic but it would seem that their chief failure lay in the neglect of experiment. Perhaps the most striking proof of this is the fact that they devised no instruments nor apparatus of importance to aid them in their observation. He who experiments, of very necessity exercises all of his ingenuity and mechanical skill to devise contrivances which will aid him in reaching his cherished goal.

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[1] Tyndall: "Religion and Science," Brit. Assoc. Adv. of Science, 1873.

Modern Methods.

The sequence of methods which in the hands of the modern man of science has enabled him to achieve such success in the study of nature is as follows: There must first be observation and then a logical classification of the facts or phenomena observed. By deductive logic the causal relations are sought out and found ; by inductive logic the underlying law is reached. Each step is tested and proved by all conceivable experimentation, much of it of the most ingenious description. These are the tools placed in his hands by the ages.

Failure of the Greeks.

The Greeks used with masterly skill their one tool, deductive logic, but it was powerless to lead them to correct conclusions when the observations were faulty and the touchstone of experiment was not applied. Perhaps no single sentence can better explain their failure than the following taken from a letter of Epicurus to Herodotus :[1] "For we have still greater need of a correct notion of the whole, than we have of an accurate understanding of the details." The first step in natural knowledge as laid down by Epicurus,[2] namely, that from appearances we must advance to their hidden causes, from the known to the unknown, is correct in principle but was poorly followed by him and his pupils. Furthermore, how could accuracy of observation be expected when it was laid down as a principle that what immediately affects our senses is not the object itself, but a picture of the object and these pictures may be innumerable, a different one being the cause of each sensation. Though these pictures, emanating from the same object, may be nearly

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[1] Diogenes: Laertius Epic., 24.

[2] Diogenes: Laertius Epic., 33.

alike, it is possible that they may differ. If the same object appears different to different observers, it is because different pictures must have affected their senses. It is not our senses that are at fault, then, in case of mistakes, but our judgment in that it draws from pictures unwarranted inferences as to their cause.[1]

Others of the philosophers would divest themselves altogether of observation or sensation and trust to logic alone as the means of acquiring knowledge and finding out the truth.

Arguments of Zeno.

In this connection the famous arguments of Zeno against the possibility of motion may well be repeated here as exhibiting the character of the logic by which these philosophers reached their conclusions.[2]

1. Before the body that is moved can arrive at the goal, it must first have arrived at the middle of the course ; before it reaches this point, it must have arrived at the middle of the first half, and previously to that at the middle of the first quarter and so *ad infinitum.* Every body, therefore, in order to attain to one point from another must pass through infinitely many spaces. But the infinite cannot be passed through in a given time. It is consequently impossible to arrive at one point from another, and motion is impossible.

2. This is the so-called Achilles argument. The slowest creature, the tortoise, could never be overtaken by the swiftest, Achilles, if it had once made a step in advance of him. For, in order to overtake the tortoise, Achilles must first reach the point where the tortoise was when he started; next the point to which it had pro-

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[1] Zeller: Stoics, Epicureans and Skeptics, 431.

[2] Zeller: Pre-Socratic Philosophy, 620 et seq. Aristotle Phys., 6, 9.

gressed in the interval, then the point which it attained while he made this second advance, and so on *ad infinitum*, But if it be impossible that the slower should be overtaken by the swifter, it is, generally speaking, impossible, to reach a given end and motion is impossible.

3. So long as anything remains in one and the same space, it is at rest. But the flying arrow is at every moment in the same space. It rests, therefore, at every moment of its flight, therefore its motion during the whole course is only apparent.

4. The fourth argument refers to the relation of the time of movement to the space which has to be traversed. According to the laws of motion, spaces of equal size must be traversed in equal time if the speed is equal. But two bodies of equal size move past one another twice as fast, if they are both moving at equal speed, as if one of them is still and the other with the same motion passes by it. Hence Zeno concludes that in order to traverse the same space—the space taken up by each of these two bodies—at the same speed, only half the time is necessary in the one case that is necessary in the other. Consequently, facts here contradict the laws of motion. These arguments, it may be added, were picked to pieces by Aristotle and it is not necessary to comment upon them here.

Contributions of the Ancients.

Sifting the chaff from the wheat, the gain in distinct ideas as to the nature of matter may be summed up as follows: The idea of elemental substances had been grasped—not just such elements as the chemist of to-day knows—yet elements out of which all things were made, the principles of things, elements it is true with interchangeable properties and capable of transmutation. The existence of atoms had been well thought out. They differed in weight and form and magnitude; they were in incessant motion; compounds were formed by their union and motion conferred upon their compounds.

No place of rest is found
To primal bodies through the vast profound,
And finding none, they cease not ceaseless rounds.
Part forced together, wide asunder leap:
From closer blow part, grappling with their kind,
In close affinities unite and form
Bodies of various figure—varied form diverse.[1]

Again:

For infinite atoms in a boundless void,
By endless motions build the frame of things.[2]

All things are made up of these atoms. In their compounds they do not touch but are separated by void spaces. These atoms were not subject to wear and could not be destroyed. Therefore, long before the time of Lavoisier or of Maquenne, matter was declared indestructible.

Nature reserving these as seeds of things
Permits in them no minish nor decay;
They can't be fewer and they can't be less.[3]

Referring to compounds Lucretius writes:

Decay of some leaves others free to grow
And thus the sum of things rests unimpaired.[4]

The store of elements material
Admits no diminution, no increase.[5]

Among other views of the Greeks which did not fall far short of the truth as it is held at present are some of the surmises as to chemical affinity. Further, the un-

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[1] Lucretius: Trans. by Johnson, Book I., 80.
[2] Lucretius: Book I, 63.
[3] Lucretius: Book I, 57.
[4] Lucretius: Book II, 79.
[5] Lucretius: Book II, 86.

changeable nature of natural law was recognized, though this did not prevent a belief in the most infinite mutability and variability of natural phenomena. The existence of ether, or the *quinta essentia*, was and is still assumed as a necessity for the explanation of various phenomena. Lastly the great thought of the harmony and essential unity of nature was dreamed of as it is dreamed of to-day.

CHAPTER II.

From the Greek Philosophers to Dalton.

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FROM THE GREEK PHILOSOPHERS TO DALTON.

It is as if one stepped from the glow of a well-lighted room into the darkness of the night, to pass from the culture and brilliancy of the Greek schools to the centuries which followed their decay. For many generations there were no new theories and speculations concerning the constitution of matter or the nature of the universe, but only imitations and repetitions of the logic and thought of the great masters. Among these teachers who were imitated towered Aristotle, and gradually he so dominated philosophy as to be the unquestioned authority to whom all appeal was to be made. Such conditions tended to decadence rather than to progress.

A closer examination will show that this state of affairs was rather to be expected. All that could be learned by deductive logic had been gleaned so far as it was of value. The greatest height attainable by this means alone had been reached. This the Greeks had accomplished in little more than two centuries. The refining and polishing of this material yielded nothing new, nor could it add to the stability of the foundation. The theorizing had gone far beyond evidence, and something else was needed to settle the great questions which had been raised. It is not strange then that further efforts along this line produced no master spirits to take the places of the giants lost.

Development of Experimental Science.

Century after century seemed to slip away without leaving a trace of progress. But this view is found to be scarcely true when tested by another standard. The slow development of experimental science, so largely neglected by the brilliant thinkers of Greece, was taking place. Many things had conspired to make this difficult. The fact that it had been ignored by such men fostered prejudice against the work. Knowledge of nature, they had said, was to be gained by introspection and logic (microcosm) rather than by observation of external phenomena (macrocosm). Material experiments were left to quacks and charlatans: to those who sought to deceive others rather than to find out the truth: to those who would learn the secrets of nature for their own enriching or for wonder-working. The pathway upward was a long and dark one. Instruments must be provided to magnify the range of the senses and multiply man's powers. Apparatus must be devised and methods of research worked out. There could be little community of work in all of this, for the workers suspected and often hated each other; little clear and direct transmission of knowledge, for the ignorant and envious persecuted any who laid claim to knowledge beyond the common ken. It is, of course, to be questioned whether there would have been any workers or progress without the attraction of the chimeras followed, such as the transmutation of base metals into gold, the philosopher's stone and the elixir of life. The pursuit of a vision or a superstition has led men to many of their greatest discoveries and bravest achievements. It does not seem probable that in the first centuries after the birth of Christianity many would have sought for truth if the reward consisted solely in its discovery.

There was much of superstition and mysticism among these workers. The old Greek idea of an overruling Necessity or Fate largely influenced them. On the walls of their laboratories was inscribed the legend, *'Ανάγκη*, and the "Ora, Labora" placed on other walls meant a servile effort at appeasing a god who had the power and might have the will to nullify all of their labors. There have been others who have bowed down to this fetish Necessity in later times, but Huxley has well stated the position of the true man of science: "Fact I know; and Law I know; but what is this Necessity save an empty shadow of my own mind's throwing."[1]

As for the training of young and enthusiastic scientific workers, such a thing was not dreamed of except in so far as it was necessary to initiate some favored apprentice, and most of the work was done in secret. Indeed it was not until a Liebig arose and the second quarter of the 19th century had come that laboratories were thrown open to any and all who chose to take advantage of them, and Liebig met with jeering and opposition in working this great reform.[2] Until that time, special influence was necessary to secure for an ambitious young man the opportunity to devote his energies to such work.

The struggle upwards then to the light seems drearily slow. It took centuries for a telescope and microscope to be invented and a spirit lamp and balance to be brought into general use in chemistry. Generation followed generation before a Keppler was born to discover the laws that govern the movements of the planets and the harmony of the universe; or a Torricelli to devise the experiment which should settle, in part, the old dispute as to the existence of a vacuum. It was more than 1900 years from Aristotle to Paracelsus who should cast off the dwarfing bondage to authority which made all science but slavish imitation.

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[1] **Huxley: "Physical Basis of Life."**

[2] **Roth, "Justus von Liebig: Sammlung Chem. Vort.," III. 166.**

A Galileo was needed to correct the erroneous views as to the sun and the earth and give release from some of the ridiculous theories of the ancients, and a Linnaeus to restore and improve the system of Natural History. After nearly two millenia a Bacon and then Comte added the last of the needed tools for man's equipment, namely, inductive philosophy, though this is but the logic of common sense, as Huxley says. Aided thus by the accumulated knowledge and discoveries of many centuries, it became possible for one equipped with even moderate mental capacity to make great advancement, and for a Newton to read deep in the book of Nature.

Eclipse of Knowledge.

It must be borne in mind that during much of the earlier portion of the dark ages, there was actual loss or eclipse of knowledge. Superstition and ignorance replaced the better understanding of the ancients in many cases of interpretation of natural phenomena. Thus Hoefer gives[1] certain examples to show this retrogression. All the world at present knows of the accidents caused in mines by asphyxiation. The ancients explained this as due to the existence of irrespirable airs, which they said extinguished the lamps of the miners at the same time that they destroyed life. The alchemists, however, did not speak of irrespirable airs, but of malignant demons who, wishing to put a stop to the work in the mines, treacherously slew the miners. Again, as to the cause of the ascent of water in a pump, Vitruvius said it was due to the air, though he failed to give any demonstration of its working. The physicists of the middle ages ascribed it to nature's abhorrence of a vacuum, which was also one of the ancient theories.

[1] Hoefer: "Histoire de la Chimie," 2.

The Alchemists. Returning to the study of the atom, it will be found that the practical workers, the Grecian alchemists and those of the middle ages did not so much as take into consideration the atomic theory. Berthollet states[1] that the word 'atom' is not to be found in the Greek alchemical manuscripts except in one or two doubtful passages. The alchemists, by unvarying tradition and expressed theories, attached themselves to the doctrines of the Pythagorean school as taught by Plato in Timaeus, and this was true down to the close of the 18th century. A passage in the compilation of ancient wisdom given by Isidorus of Seville (636 A.D.) would seem to indicate a degeneration of the atom into the ultimate, or indivisible unit of various classes of things. Thus he says :[2] "There are then atoms in bodies, in time, in number or in words"—meaning in these latter cases the minute, the number one, and the letters with which words are written. Stephanus[3] (620 A.D.), whose works consist of nine lessons addressed to Emperor Heraclius and a letter to Theodorus, writes in Lesson VI of the indivisible atoms which constitute all bodies. Only a few scattered references of this character are to be found in the literature of the early centuries of the era.

Opposition of the Church. The domination of the church militated against speculations as to the origin and nature of the universe, fearing that the mechanical, or indeed any general explanation of the phenomena of nature, would remove the necessity for a divine creator and so would eliminate God from the universe. Thus Thomas Aquinas considered all such striving a sin, except in so far as it was directed toward

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[1] Berthollet : "Les Origines de l'Alchimie," p. 263.

[2] Isidorus : "Orig. de Mundo," Lib. XIII. Cap. II.

Berthollet : " Chimie des Anciens," p. 289.

a better knowledge of God. The study of nature was at one time largely turned over to those who would use it in their profession of healing and thus *physicus* became the synonym of *medicus* and from this came the English word physician. In the writings of the fathers of the early Christian Church, a favorite object of attack was the atomic theory of the ancients and contumely was heaped upon it. Lasswitz[1] says that they could not repeat often enough that busying oneself with physics, as the Grecian philosophers had done, was not only a vain exertion which could only turn upon the unnecessary and useless, and in its object was far beyond the measure and strength of the human mental grasp, but that it included a danger for the safety of the soul as the examples of Leucippus and Democritus proved who were led away into atheism. The views of the Atomistic school were represented as being very absurd and the atomists themselves as blind and pitiable creatures. This mockery of the theory was particularly directed at the supposed motion of the atoms, their meeting, combination, and thus the formation of the universe. Of course the point of offense was, as has been stated, the materialistic view of nature, the elimination of a designing power in creation and the ascription of the formation of the universe to the fortuitous concourse of atoms. This attack was first from the side of the defenders of the ancient deities and was taken up more vigorously and successfully by the Christian Church. Many of these writers contented themselves with abuse and ridicule. Thus Dionysius Alexandrinus[2] wrote: "Ye blind; do then the atoms bring you snow and rain so that the earth and all living nature may bear nourishment for you? Why then do

[1] Lasswitz: "Geschichte der Atomistik," I, 13.

[2] Lasswitz, I, 16.

you not fall down before your atoms and offer them sacrifices as to the lords of the harvest? Ye ungrateful ones, not once from the many gifts which ye have received have ye offered them the first fruits." Eusebius, in his *Preparatio evangelica*, quotes with approval this tract of Dionysius, not troubling himself over its lack of argument. Lactantius,[1] in the Fourth Century, did make a crude attempt at a scientific refutation of the Atomistic doctrine. "Who has seen, felt or heard these atoms?" he asked. He saw in the diversity of nature an argument against the formation of the universe out of particles. Again, if the atoms were light and spherical they could in no case hold firmly to one another so as to form a corporeal substance. If rough or hooked so as to hold on to one another then they must be divisible into parts. Do water and fire also consist of atoms as maintained by Lucretius? Then how is it that fire is kindled even in the deepest cold, when a glass globe filled with water is held between the sun and tinder? Were the "seeds of fire" in the water? Certainly they were not in the sun, for that cannot set tinder on fire even in midsummer. As to animals, if you grant that limbs and bones and nerves and blood are made up of atoms, what about perception, thought, memory, spirit? By the bringing together of what "seeds" can they be formed? "By the finest," says Lucretius. Then there must be coarser, argues Lactantius, and in that he sees an admission of divisibility. His chief argument is directed against the possibility of a mechanical, accidental meeting of senseless things, and thus the production of the beautiful harmony and adaptative of the universe, without any supervising or directive agency.

This style of argument was much better than the ridi-

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[1] **Lactantius: "De ira Dei ad Donatum." Lsw.**

cule, abuse, and misrepresentation which has been adverted to. The theory of the atomists was in truth only what would be called in these days a working hypothesis. The verdict concerning it must unquestionably have been "not proven," and the arguments of Aristotle had really placed it in a very questionable light. It offered, however, apparently such a simple means of explaining difficult problems that its advocates had pushed its use and interpretation to extremes which rendered them exceedingly vulnerable. But ridicule is easier than finding out the defects in an opponent's arguments, and besides it requires no learning and is after all more effective than argument with the ignorant masses.

Augustine writes[1]: "It had been better had I never heard the name of Democritus than that I should think with pain that once a man was considered great, by those of his time, who believed the gods were pictures which flowed from fixed bodies without being themselves fixed." He cites the arguments of Cicero against the Epicureans and his expositions coincide with those of the great Roman. They complement also the arguments of Lactantius in attacking the perception and recognition theory of the atomists, among other things asking very shrewdly how, granting the existence of atoms and the consequent claims of the atomists, is it possible for atoms to think atoms or in any way to become cognizant of them?

Of course these old-world disputations have little interest now and it has been necessary to go into them so far, only to make clear one of the reasons why men cared little to take up this theory, either to seek to confirm it or to use it in explaining the varied problems presented by nature. The all-dominating Church frowned upon

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[1] **Augustine · "Epistola ad Dioscorum" Op. Tom., II, 248. Lsw.**

many such inquiries. At the conclusion of his argument mentioned above, Augustine apologized for "touching such filth. Why should the Christian trouble himself to find any outward explanation of the marvels of nature? Leave that to the heathen." Going still farther, in 1245 the Dominican order forbade the study of physics. So far as philosophy was cultivated it was that of the Neo-Platonic school which offered little for the scientific answering of questions as to the nature of things but the age asked few questions and cared little for scientific answers.

Kinds of Atoms.

In the seventh and eighth centuries we have only a stray reference or two to atoms and most of these have already been cited. This theory of the ancients had almost passed from memory and the word had received new meaning. It has been mentioned how Isidorus, of Seville, whose writings formed the thesaurus of culture and knowledge of his times, distinguished between atoms of bodies, of time, of number, and of written language. Here the word meant the ultimate unit, distinct and indivisible. But he also recognized the ancient use of the word. "The philosophers call atoms certain particles of bodies so exceedingly small that they cannot be seen nor can they be divided. They are said to fly in restless motion through the void of the entire world and are borne hither and thither like the dust in the sunbeams so that out of them all trees, vegetables and fruits spring, also fire, water, and everything come from them and consist of them according to the belief of certain of the heathen." This passage and the distinction between the varieties of atoms are quoted by Venerable Bede.[1] He divides the hour as follows:

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[1] Venerable Bede, Op., I, 90. Lsw.

$$1 \text{ hora} = \left\{ \begin{matrix} 4 \text{ puncti solis a } 2\,\tfrac{1}{2} \text{ minuta} \\ 5 \text{ puncti lunæ a } 2 \text{ minuta} \end{matrix} \right\} = 10 \text{ minuta} = 40 \text{ momenta} = 22{,}560 \text{ atomi.}$$

The word atom entered more and more into common speech to signify anything very small and not farther divisible. The musician, the astrologer measured by atoms; the grammarian spoke of them, and in general the word denoted a moment, a sand grain, a particle of dust, etc. The word had lost its metaphysical meaning and the philosophical theory was no more thought of.[1]

General Theories.

It would be going too far afield to attempt to follow the rise and progress of philosophical discussions and schools during the middle ages. While these bore upon the question of the nature of matter and the universe, and have their value from the standpoint of the philosopher, they brought no confirmation or refutation of the doctrine of atoms nor did they advance the knowledge of nature and so they may well be omitted here. As to general theories the four elements of Empedocles were generally accepted as the components of all things, and their nature was discussed. The principle of the indestructibility of matter, so clearly stated by Parmenides and Epicurus, was reiterated by some though apparently forgotten by others. Thus Adelard, of Bath,[2] said: "Nothing is ever entirely destroyed. When a combination of particles with others ceases, their existence does not cease but they go into another combination."

In the "Elementa Philosophiæ" of William of Conches, there seems to be a very careful avoidance of the word

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[1] Lasswitz: "Gesch. d. Atomistik," I, 90.

[2] Adelard of Bath, Translated by Stahr, quoted by Lasswitz, I p. 71.

atom and yet the idea is well preserved. All bodies consist of elements. By an element one must understand the simplest and smallest particles of a body. These elementary particles (*particula*) are invisible and indivisible except in thought. He made use of the word *homiomera*, showing his knowledge of the writings of Aristotle and the source of his ideas as to matter. He stated further that the elements were not properties but matter. Properties reside in the elements but are not the elements themselves. The elements are rather simple particles which determine the properties of bodies by their coming together. These are the *prima principia*. They were first created and then out of them all other things.[1]

Influence of Aristotle.

These and a few other references during these earlier centuries up to the 12th are the only evidences of any effort to keep alive the doctrine of atoms. With the introduction of Arabic learning into Europe came the wisdom of the ancients, which they had preserved, and the chief source from which they drew their learning was Aristotle. The practical disappearance of the atomic hypothesis may be attributed to his influence. He was the arch-antagonist of the atomists and with the predominance of his philosophy over schools, backed by the opposition of the Church to atoms and everything else that smacked of materialism, the atomic hypothesis practically disappeared from view for several centuries, despite growth in mathematical and physical knowledge which should have supported it. The opposition of Cicero and Seneca and especially of Galen among the ancient authorities cannot have failed also to have had great weight.

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[1] Wil. de Conchis: "Elem. phil.," p. 209. Lsw.

Arabian Theories.

The study of Aristotle by the Arabians did not entirely prevent their including the idea of atoms in their philosophy, yet it led to certain modifications of the doctrine so as to attempt to meet the objections of Aristotle. Their atoms were without magnitude yet having position. By the definite position to one another form was given and the power of occupying space. It must be remembered that the Arabians were especially noted for their cultivation of the mathematical sciences. Now in their theory all of their atoms were alike, their number being changeable at the will of the Creator. In order that they might move there must be vacua, otherwise if all space were full of atoms some would penetrate others in moving. Each atom was inseparable from certain conditions as smell, color, motion or rest. Magnitude, however, is not a condition but belongs to compound bodies only. Life and perception were among the conditions inseparable from the atoms and here we have the origin of the hylozoic views of the alchemists and early chemists. There was difference of opinion as to whether the atoms were gifted with thought, knowledge and souls. These views are instructive chiefly as showing a transition state of the atomic doctrine and the effort so to modify and mold it as to accord with the accepted views of their religion, and to disarm antagonism. The scholiasts, who followed the Arabians and Arabists, chiefly engaged in word-splitting and in the setting-up of arbitrary ideals which led away from nature. "It is better to dig into nature," says Bacon, "than to build upon your abstract ideas. It was the analysis of nature which occupied the school of Democritus and so it penetrated deeper than others into nature."

Mathematical Views.

As mathematical knowledge grew, some interest was shown in attempting to prove the Aristotelian view that matter was continuous. The particles of matter were usually regarded as mathematical points. Roger Bacon sought to solve the problem by a mathematical search for a body of regular form which could fill space without leaving any vacant spaces. He believed this was possible for hexahedra, tetrahedra, and octahedra. This would conform with the Platonic hypothesis so far as the cubical earth particles, the octahedral air and the tetrahedral fire were concerned, but not as to the others and after all this is nothing more than an expression on the part of Bacon of the belief common to all the alchemists. Bacon's being, however, only a partial acceptance of the Platonic doctrines and not excluding the possibility of a vacuum, differed from the views of all the scholiasts who were agreed as to the impossibility of a vacuum.

Conditions of Elements in Compounds.

Aristotle had indicated his belief that the elements when they unite to form compounds, though suffering change of properties, did not cease to exist. He left it to be decided whether they existed actually or potentially. This point was taken up and discussed with zest by the Arabians. Ibn Sina contended for the actual existence, the persistence of the unchanged form. Averrhoes thought that the form of the elements must also be changed. If the compound derived its properties through the loss of those properties to the elements, then it could have no substantial form unless those of the elements were changed. The influence of the Pythagorean ideas is easily to be traced in this argument. Albertus Magnus adopted the hypothesis of Avicenna, that an element has a double existence. In the first state, when free, it possessed all of its natural characteristics; in the second, or bound (ligatum) state it is influenced by other elements. Hence, in compounds, the element, although bound, is the same element, though only in potentiality. This was rejected as an explanation by his pupil, Thomas Aquinas, and his opinion as that of the Angelic Doctor prevailed. His view seems to have been that the influence of the elements upon one another resulted in properties which are the means of the others and the forms are included in these properties. Duns Scotus (1308) maintained that the elements lost their existence when they entered into combination, but in that act they took on a higher existence. The combination also did not come about by the self-interaction of the elements, but was brought about by some general and natural agency, thus opposing the view of a life or soul in the particles themselves. From the 14th century on, the number of adherents to the doctrine of the persistence of the elements increased, adopting either the view of Albertus Magnus or of Averrhoes.

Van Helmont and the Corpuscular Theory.

Passing by the indeterminate discussions of the next three centuries, there is reached in the teachings of Van Helmont (1577–1644) a transition to the corpuscular theory. His first great service consisted in his maintaining the existence of two primal, unchangeable and non-transmutable elements, water and air.[1] But it is from water that he believed most substances to have been formed, and it is not perfectly clear always as to the part played by air in his theory. His most important contribution to the corpuscular theory is in his

[1] Van Helmont: "Causæ et Initia," 23, p. 29; Lasswitz, I, 344.

representation of what takes place in the changes of water into steam, and in the distinction drawn by him between vapor and gas. In this latter case, he says the difference lies in the arrangement of the fundamental substances in their smallest particles. This is very crude, however, and has only a far-off resemblance to the allotropism or isomerism of the present day. Van Helmont makes frequent mention of the motion of atoms, but by this term meant merely very small particles without any reference to their indivisibility.

Giordano Bruno, 1548-1600. From a purely metaphysical standpoint, Bruno did much to pave the way for the resuscitation of the corpuscular theory. Matter was to him no longer the passive substratum of all nature, as imagined by Aristotle, but all possible things at once, embracing in itself all forms and dimensions. Matter was a unit, in eternal motion, one and inseparable with force in harmonic order and in organic and necessary development. The search after unity was a necessary condition of all knowledge. There must be in all things an ultimate, smallest, indivisible unit, a minimum, of which all things consisted. This was not merely the physically smallest and indivisible of space, but the absolute, simple, and unchanging. This minimum Bruno also called "monad," a word which originally meant the unit of numbers, but which became later a favorite term in metaphysics. The corporeal minimum is the atom or primordial body. For this he decided the only possible form was the spherical.

The hypothesis of spiritual matter, a *quinta essentia*, or subtle stuff, which was not properly body nor yet spirit, since in the one case it could not be perceived by the senses, in the other case it occupied space; a something then which occupied an intermediate position between corporeal and spiritual matter, an ether or a spirit; such an hypothesis was wide-spread among the ancient philosophers and was accepted by Aristotle. This ether Bruno identified with the vacuum of Democritus. It filled all space between bodies and between the spherical atoms. In this, bodies could move without restriction. It was the bearer of all force. It was the world-soul, the dynamic of nature. Herein was it different from the modern conception of ether as simply a mechanical medium. It must be borne in mind that Bruno was not a physicist but a poet, and his view of the universe was largely poetical. That he looked upon solid bodies as consisting of atoms did not spring from a physical necessity for explaining phenomena, but was merely the outcome of his metaphysical doctrine of monads, to which we are indeed indebted for a number of fundamental conceptions, but rather in the realm of philosophy than of natural science.[1]

Lubin, 1565-1631.

In Lubin the corpuscular theory had a noteworthy defender who maintained the logical necessity for the conception of atoms and endeavored to meet all the objections urged by Aristotle and the Scholiasts. The basis of his arguments lay in the impossibility of conceiving the infinite. Since continued division could have no end and was, therefore, infinite and inconceivable, all substances in nature must consist of indivisible atoms.

Francis Bacon, 1561-1626.

Francis Bacon, in his "Cogitationes de Natura Rerum" did much to strengthen the tendency toward a return to the atomic hypothesis as a necessity for the explanation of natural phenomena, and as a basis for physical science.

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[1] Lasswitz: "Gesch. d. Atomistik," I, 396.

His work was in the main mathematical and metaphysical. In the first place he restated the dogma of the constancy of matter. Nothing could come into being out of nothing, and something could not pass away into nothing. The atomic idea might be grasped in either of two ways. An atom might be conceived as the utmost bound of the division of bodies, or secondly as a body which contained no empty space. It is manifest that division can go far beyond the detection of sight or of sense, for odors are invisible, yet must consist of particles of the bodies, for they can be rubbed or washed from articles to which they have fastened. In his *Novum Organum* he seemed like Leibnitz, to have gone over from the atomistic view to that of matter as an elastic fluid. He no longer spoke of a limit of divisibility and left the question of empty space undecided.

Daniel Sennert, 1572-1637.

In Daniel Sennert we have the first man, trained to experimental science, who arose as a defender of the atomic hypothesis since the time of Democritus. He was professor of medicine at Wittenberg and one of the most skilful chemists of his day. The principle upon which he worked was that the observation of the whole alone was no aid to progress. One must descend to the details and observe closely nature itself. For the theoretical explanation he made use of the theory of atoms. As proofs that bodies consist of aggregations of atoms he adduced the formation of smoke by burning bodies and the process of sublimation. This latter was regarded also as a proof that the fine particles did not change in nature. Again, solutions of substances, as in mineral springs, may be perfectly clear and transparent, yet incrustations form from the separating out of very minute particles which must have been suspended in the liquid yet invisible. Solution of metals in acid or salts in water must then be due to a division of the substance into atoms. Changes in natural substances are an exchange of outward form while the particles remain the same and unchanged.[1] For him it was a necessary conclusion, he wrote later, that there should be certain simple bodies out of which compound bodies were formed, and into which they could be again resolved. These simple bodies were physical, not mathematical minima. He gave the various names for them: minima naturæ, atomi, atoma corpuscula, *σωματα αδιαίρετα*, corpora indivisibilia. These are the ultimate subdivisions beyond which nature cannot go and again are the beginnings of all substances in nature. He further distinguished between the atoms of the elements and atoms of compound bodies. Thus there are four elementary atoms, those of fire, air, water and earth. The second class were those into which compounds were divided in dissolving and mixing, and by their combination new bodies were formed. The "forms" of the atoms, which determine the species of things, remain unchanged. Thus, in alloying gold and silver the atoms unite most intimately but each retains its distinct form. Gold remains gold and silver silver, as may be seen by dissolving the silver away with aqua fortis, leaving the gold in the form of a powder. The "form" of the atom did not refer to magnitude, as the atom possessed neither magnitude nor divisibility. By the concourse of atoms the most widely differing bodies could be formed. The states of aggregation were also explained by the theory of atoms. Clouds are not continuous bodies but made up of thousands of myriads of atoms, which, in forming rain and snow, again

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[1] Sennert: *De Chymia*, XII, 230, 231 (1619), Lsw.

unite. Condensation consists in the reuniting of atoms which had been separated. So when water evaporated it did not change to air but into its own vapor, as mercury sent out mercury vapor. Sennert had begun with a belief in the transmutation of the elements. It would seem that a change had been wrought in his views by the study of the atomic hypothesis. The belief in the unchanging nature of the elementary particles and the impossibility of transmutation was growing and was necessary as a foundation for all true theorizing in chemistry. As to the cause of the concourse of atoms, Sennert could not think of it as fortuitous, as was held by Democritus and his followers, but as being due to the influence of the "forms," that is to say, the nature. God had so ordered these forms that the atoms fitly arranged themselves in the compounds.

Other Theorists. It is not needful for our purpose to speak at length of the theories of Gorlaeus (1520), or of Basso (1621), and other worthy adherents of the rising school of the atomists nor can the task of deciding their influence upon one another or upon Sennert be undertaken here. Suffice it to say, that, though misled in part by erroneous views, they were able and zealous in the revival of the atomic philosophy. Many adherents were being won. In 1624, in Paris, then the center of learning, began the agitation for atomistic views of nature. A public debate was announced to be held by the defenders of these doctrines, and certain theses were distributed against the views of Aristotle and the Peripatetics. These were condemned by the church and the punishment of the law was threatened against all who had aught to do with such doctrines. Three of the agitators, De Claves, Villon, and Bitault, were banished from the city of Paris.

Galileo and the Italian School.

Probably the most potent factor in the renaissance of the doctrine of atoms and in so modifying it as to infuse new and lasting vitality, was the progress in the science of mechanics and physics. A new idea of energy had grown up. This idea of energy was imparted to the motion attributed to the atoms. This motion, as conceived by Democritus, was merely a change of place, and though this brought about a meeting of the atoms and so influenced their combination, the idea of an intense energy resulting from the motion and residing in the atoms was lacking. This idea of energy is to be seen in the works of Leonardo da Vinci, of Benedetti and of Galileo. It was the office of the latter to create, one may almost say, the new science of physics. He considered motion an original property of unchangeable matter and that the physical properties of this matter were to be explained by the motion of the particles. Thus, heat is explained by him as only present in matter as a motion of the particles. The mere presence of heat particles is insufficient; they must be in active motion.[1] A substance can contain many fire particles and yet be cold unless these particles are freed by motion. On account of their fineness and great velocity they can overcome the cohesion of particles, decompose the body, or melt it, etc. Galileo would not admit the possibility of a vacuum. But the most valuable part of Galileo's work is the application of experiment to this problem of the nature of matter and its reference to such mathematical and mechanical principles as were known to him.

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[1] Galileo: "Op.," II, 341, 342. Lsw.

Descartes and the Corpuscular Theory.

The atomic hypothesis was now almost completely merged in the corpuscular theory, in which the existence of particles was still assumed, but these particles were supposed to be indefinitely divisible, and matter was generally considered continuous. This has been noted as the view of Hero, of Alexandria, and of Asclepiades, of Bithynia. It formed a partial adaptation of the views of Aristotle and of those of the atomists without conceding the crux of the atom's indivisibility. These views received their highest development at the hands of Descartes. He was certainly one of the deepest thinkers and most brilliant men of the 17th century, and his writings had great influence upon subsequent thought as well as upon his contemporaries. He was thoroughly trained in the mathematics and astronomy and mechanical physics of his day. He wrote works on physics, discovered the law of refraction of light, the explanation of the rainbow, knew well the work of Keppler and acknowledged its influence upon him, and knew and quoted Harvey upon the circulation of the blood. He was the first to suggest the explanation of the experiment of Torricelli, stating that the mercury was sustained by the pressure of the air, and suggested to Pascal the crucial test of this explanation by making use of the barometer to measure the heights of mountains. The work of Galileo and of Gassendi was known to him and he was indebted to the theories of Sennert, Gorlaeus and especially of Basso. These theories were announced in the years 1619–1624. In the latter year a decree was made public in Paris forbidding the promulgation of atomistic or corpuscular theories under pain of death, so the theory of Descartes was not made public until after he had left

Paris. Thus it may be seen that such a thinker as Descartes was prepared to make the best use of a very wonderful age in which most important discoveries and progress in science were being made. The method made use of by Descartes was the analytic, and, in contradistinction to the methods of the ancients, he believed that a knowledge of nature was to be obtained only through impressions gained by the senses, the chief of these impressions being those of extension and form.

The conclusions reached in his philosophy were that there was no vacuum, that matter was infinitely divisible and that there was but one universe, infinitely extended yet composed of one and the same kind of matter. For the idea of atoms there was substituted that of small particles or corpuscles, for these were needed in order to explain physically many phenomena. These particles were further divisible, yet were not the secondary particles or molecules of Sennert and Basso, a theory of which he strangely made no use. It was further supposed that these particles were in constant motion as were the atoms of Democritus, only this idea of motion was extended. A particle might have many motions at the same time, as the wheel in a watch, carried by a man upon a ship, would have its own motion, and that of the man, the ship, the sea and the earth. Motion meant energy as well as mere change of place. There were three elements—fire, air and earth. Originally all nature was filled with one material, homogeneous, fluid, continuous. At creation, God divided this into different particles and it would be limiting the power of the Deity to say that there were indivisible particles which he could not subdivide at will. To these particles he gave specific motions which thereafter distinguished them and gave the different elements.

Thus there was one original source of the elements and their genesis was brought about by motion. The original form of the particles was not of consequence; in their motion they rubbed together and so lost edges and angles and assumed such form as was necessary to completely fill space. They were really conceived of at times as fluid and plastic by Descartes, and at other times as rigid, and his system offers a number of such contradictions. His explanation of the striking of fire by means of a flint and steel may serve to exemplify his manner of reasoning. The hard particles of flint find themselves suddenly surrounded by the ball-like fire particles and flame follows.[1] As to the existence of a vacuum, he regarded such a thing as unproved and its assumption as unnecessary for the explanation of phenomena. The supposed pores of bodies are filled with particles of the fire element which are not atoms but an extraordinarily fluid and fine substance. In a letter to Mersenne (1630) he wrote: "If you now grant me that there is no vacant space, as I think I am able to prove, then you are forced to grant that these pores (in gold, etc.) are full of a matter which easily penetrates everywhere."

The Vacuum of Torricelli.

It may seem strange in these days that the views of Descartes as to the existence of empty space were so little influenced by the famous experiment of Torricelli which was apparently so conclusive on the question. Especially might this cause surprise when one thinks that Descartes was the first to suggest that the column of mercury was upheld by the weight of the atmosphere. This experiment of Torricelli with the mercury column and the empty space above attracted a great deal of attention and

[1] Descartes: "Principia," IV, 84, Lsw.

was repeated in many places, arousing much interest because of its theoretical bearings. It was modified in various ways and subjected to acute testing and reasoning. The general opinion was, however, that it had by no means proved the existence of an absolute vacuum. It really had very little direct influence at the time upon atomic views because one was not forced to believe the space above the mercury absolutely empty, but could assume the presence of a sufficiently fine matter. Still many adhered to the belief in a vacuum. The most important contemporary of Descartes retaining this view was Gassendi, who did not base his assumption of the vacuum, however, upon the Torricellian experiment but upon the necessity for a vacuum as an explanation of many physical phenomena. Thus, it was needed to explain the expansion and contraction of air and, in general, the action of heat and cold upon bodies, or again, to explain the varying specific gravities. He regarded it as an explanation of the solution of a solid in water. Thus salt particles are taken up and held between the particles of water, *i.e.*, in the empty spaces. If this was true, then when water had dissolved all of the salt it could hold, there should still be empty spaces in which something else could be held. This view he believed he confirmed by the experiment in which he dissolved an amount of alum in water already saturated with salt. For his view of matter, atoms were also necessary and these were the undecomposable atoms of Democritus.

Thomas Hobbes, 1588-1679.

Thomas Hobbes, who did so much for the advancement of physics and for its establishment as a science, seemed to return in part to the methods of the ancients in his view as to the best method of discovering truth.

In his opinion, knowledge was to be obtained with certainty only by the exercise of the reason and of logic and not from the testimony of the senses. When closely examined, however, this only meant that the testimony of the senses must be rigidly tested by the reason to avoid error and to advance truth. It was Thomas Hobbes who first maintained that geometry was the only exact science. Physics was indebted to it for all of its true progress. A science must be based upon geometrical principles. It is thus seen that he was an important factor in lifting science from the level of mere empiricism and systematized observations, and in insisting on a proper basis for theory. So far as his theories bear upon the subject under discussion they may be briefly considered. He propounded in the place of the corpuscular theory of Descartes that of an original fluid matter with particles readily slipping by and between each other. He recognized no fixed, rigid atoms or particles. There was no need for a vacuum and he denied the existence of such in the barometer. The existence of an extremely fluid ether was assumed by him, which had no other motion than that received from the bodies moving in it.

It is clear that it was mainly the physicists who were concerned in the reviving of the atomic views and that it was regarded as chiefly a physical problem. It was because of their efforts to explain physical phenomena that the simple atomic theory was lost sight of for a time and that the corpuscular theory, strange admixture of atoms which were not atoms and of the continuity hypothesis, arose. Chemists from the time of Paracelsus had combatted the Aristotelian doctrines with a theory of atoms which, however, embodied much that was unscientific and was imperfectly formulated and only accepted here and there. For them the primal elements were ceasing to be substances which could be transmuted the one into the other. They thought of matter as possessed of a living creative 'force' such as is seen in the growing organisms of nature. They were opposed to a mechanical conception of nature.

Robert Boyle, 1627-1691.

Now, in Robert Boyle we have a combination of chemist and physicist and the highest type of the experimental philosopher of his day. He was most interested in the establishment of facts by experiment, and theoretical speculations were to him a secondary matter. Hence it is that his theories were not as fine spun nor extended as those of other philosophers, interesting him little beyond their capacity for service in explanation of his facts. There was for him one only and universal matter, common to all bodies, extended, divisible, and impenetrable. The differences in bodies sprang from the differences in motion. The particles possessed magnitude, form, and motion. The order or position of these particles was fixed and had to do with the nature of the body. There were two classes of particles; the original corpuscles, too fine for us to perceive, and stable groups of these particles, hard to dissociate, forming thus secondary particles. The particles of the elements, earth, water, etc., were themselves made up of these fine particles. These could further unite and give the various compounds. All bodies, even those apparently solid, have pores and these are penetrated and filled by the effluvia of other bodies. These effluvia are breathed out by all bodies, and thus every substance forms an atmosphere around it. To support this theory of the fine effluvia he adduced many facts and experiments which are of especial interest because among them the testimony of the microscope is called upon as an aid in this discussion, and further the first quantitative chemical experiment is brought to bear upon it. Ammonia, he said, gives a perceptible blue in a solution which contains only the 28,534th part of its weight of copper or the 256,806th part of its volume. This he looked upon as a proof of the power of copper to send out an exceedingly minute effluvium.[1]

Boyle was especially desirous of giving a scientific foundation to chemistry. He hoped that chemistry, laying aside the aims of the hermetic art, would acquire a new growth upwards and would contribute much, if not to the finding of the elixir, then to the ennobling of the human race and the increase in the knowledge of nature.[2] The best foundation for the new chemistry he thought would be the corpuscular theory, and hence he sought to make this theory acceptable to chemists. Boyle regarded those experiments in which a body was changed into one compound and out of this again into its original condition as among the best proofs of the truth of the corpuscular theory. Such experiments were inexplicable from the standpoint of the Aristotelian theories. One of these experiments which he most highly regarded was the reproduction of niter out of the constituents obtained by its analysis. Affinity was explained by him on the mechanical principles of the corpuscular theory. The corpuscles of sulphur form with those of quicksilver a stable compound, cinnabar, but the corpuscles of sal tartari (potash) unite yet more closely with sulphur so that they set the quicksilver free from the cinnabar. A greater affinity was to him, then, not a question of attraction but of the form of the particles, and was determined by the possibility of

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[1] Boyle: "Exerc. de mira. Subtil. effluv.," C. 3, p. 9. Lsw.

[2] Boyle: "Spec. unum atque alt."—Pref.

closer and firmer connection. It is not possible here to follow at greater length Boyle's application of mechanical principles to the explanation of chemical phenomena. Where knowledge of both principles and phenomena were imperfect, the applications were of necessity faulty. But this was a great step in advance upon the easy and meaningless attributing of all that was difficult to explain to qualitates occultae, souls, sympathies, attractions, etc. As to the strife over the existence of a vacuum, Boyle declined to side either with the plenists or antiplenists. He would not assert that the top of the barometer tube or the receiver of the air-pump was empty, but he said that it was certainly empty of air and the elaborate theory of Hobbes was false.

At this time the various attractions exhibited in natural phenomena were under consideration, and a number of theories were advanced concerning them. As has been seen, Boyle wished to substitute the property of form and the closeness of connection depending upon it for the elective affinity of chemistry. Borelli denied the existence of any attractive force or attraction in nature. His substitute seems to have been a propelling force. Thus magnet and iron are by a natural force set in spontaneous motion toward one another. This could, of course, be referred to a primal force or motion.

Vibration Theory of Hooke.

Hooke introduced the new idea of a vibration theory. The continuity of matter was maintained by him and the filling of space was looked upon as dependent not merely upon the position and size of the particles, but essentially upon the character of their swinging movements and that all properties of bodies depended upon the coincidence or interference of their vibrations. This he called the congruity and incongruity of bodies. On the hypothesis of these vibrations he based an undulatory theory of light, first suggested by Grimaldi. An example given by him may best illustrate his views as to matter. Suppose a very thin plate of iron, one square foot in area, vibrating backwards and forwards at right angles to its plane with such velocity that no other body can penetrate the space in which it moves. If this vibration measures one foot then it has the same effect as if space were filled by a cubic foot of a body appreciable to the senses. In his lecture on this subject he said: "I do therefore define a sensible body to be a determinate space or extension defended from being penetrated by another by a power from within.

Huygens, 1629-1695.

Huygens contributed much to the advancement of physics and to the return to the atomic idea. His undulatory theory of light was nearly in accord with the theory of the present day but was neglected for the sake of the Newtonian theory. His rotation theory as to gravity also served to show his experimental powers, clear insight, and acute reasoning. He assumed the existence of empty space so as to allow for motion. In his theories he also had need of a light ether and a gravitation ether, not fluid but made up of extremely fine particles. It was necessary too, that there should be solid, indivisible particles or atoms. Thus he wrote to Leibnitz: "The ground upon which I am forced to assume undecomposable atoms is this, that I, just as little as you, can accommodate myself to the Cartesian doctrine, according to which the existence of a body consists in its extension alone, and that I therefore find it necessary in order that the bodies may retain their form and resist opposing motions, to ascribe to them impenetrability and resistance against breaking and compressing. * * * * The hypothesis of infinite stability seems to me therefore very necessary and I cannot understand why you should find it so strange."[1] In considering the motion of the atoms he introduced the principles of mechanics and enunciated the laws of collision. In these there was offered an explanation of that which had disconcerted the theories of Gassendi and Galileo, and others who adhered to the kinetic theory of atoms, namely, the reality of the motion and its continuity without loss from collisions. Unchangeable, non-elastic atoms were necessary and a transmission of the force through them. For the kinetic atomists of the 17th century, then, all forces in nature, heat, light, electricity, gravitation, chemical affinity were based upon the mechanics of atomic motion and this was the fundamental principle of their natural philosophy. A change of one force into another was then entirely possible. The problem remained to refer the particular individual motions to adequate mathematical laws. The ultimate motion of the atoms could not be reached. It was possible only to decide by comprehensible mathematical formulas the observed motions. This was accomplished by Newton in the laws of gravitation.

Leibnitz wrote of Huygens: "Of all who have maintained the assumption of atoms none have done so with so great knowledge of the causes nor have contributed more to its illumination."[1] Still the theories of Huygens won but few adherents because of the opposition and overwhelming influence of Leibnitz and of Newton. But his thoughts were not lost. They exercised much influ-

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[1] Leibnitz: "Math. Schrift," II, 156. Lsw.

ence over the most thoughtful men of the time. The development of the calculus was a necessity, however, before they could yield their highest results.

Attacks of the Church.

The latter half of the 17th century witnessed a very determined onslaught of theologians and churchly authority against Descartes and the corpuscular theory. In 1663 his works were placed upon the Index Expurgatorius. In 1667 the erection of a monument in Paris was forbidden, and in the next succeeding years the Cartesian system was placed under the ban at the most prominent French universities. One of the strangest but most potent arguments used by the churchmen was that in the light of the corpuscular theory the transubstantiation dogma of the Eucharist became an impossibility. These attacks led some atomists to endeavor to bring their theories into harmony with the decrees of the church. Such efforts had no bearing on the development of this theory and have no value nor interest here. It is necessary also to pass without mention the systems of Malebranche and Spinoza.

Leibnitz, 1646-1716.

Leibnitz, largely influenced by Hobbes, in 1670, in his "Hypothesis Physica," maintained the continuity of matter, the existence of ether and the motion of the corpuscles. Matter was fluid but he overcame the difficulty experienced by Descartes in introducing solid bodies into it by calling those bodies rigid whose particles were in harmonious motion. The form of a body then was the space occupied by its moving particles. The penetrating ether was taken up by these bodies in bubbles (*bullæ*). This theory of bubbles was elaborated very fully but need not be farther referred to here. The ether present everywhere in the interstices of bodies was the exciting cause of the motion and of chemical reaction. This ether was then about the same as the Archaeus of Paracelsus and Van Helmont, the Rector of Tachenius, the Spiritus Mundi or Mercurial Principle of others. The chief service done the corpuscular theory by Leibnitz consisted in his bringing mathematical analysis to its support, as Huygens' consisted in his applying the principle of mechanics. Still it was at best only one of the possible hypotheses suggested for the explanation of natural phenomena. Much more was necessary in order that it should become the real and only explanation, based upon accurate mathematical laws and substantiated by experiment. Its plausibility won for it many adherents, some holding the true atomic view of indivisible atoms and empty spaces, others the view of a continuous matter and no vacuum, but all agreed upon the motion of the particles whether atoms or corpuscles. Some of these followers of the greatest thinkers, pressing too far in their unwise zeal that which was at best but a plausible working hypothesis, brought it into discredit and compassed its downfall as the dominant philosophical theory. With the waning of the corpuscular theory the hylozoic theories took on new life and growth. Matter was again invested with soul and life, and the world became full of the ghostly spirits.

Newton, 1643-1727.

When one comes to Newton he finds that there is no effort at formulating a complete theory on his part as to the constitution of matter, and his thoughts on the subject are scattered here and there through his writings. The problem was for the time discredited or rather looked upon as beyond solution with the knowledge and instruments at hand. He took no interest in speculations which gave promise of nothing positive, or, perhaps more truly, his interest was not aroused in that direction. Yet he borrowed much from the theories of the philosophers who had preceded him. His view of nature was that of a dynamic rather than of a kinetic atomist. In so far as he assumed the existence of rigid separate particles of matter his system was based upon the corpuscular theory, but he did not agree to the view that their interaction was due solely to the motion springing from their meeting one another. In the place of the laws, which according to Huygens regulated this imparting motion through collision, he substituted force working at a distance. He conceived of the ultimate particle as a "solid, massy, hard, impenetrable, movable particle."

"Hypotheses non fingo" was his famous saying, often quoted as showing his dislike of speculations. In his opinion, everything which does not follow out of observations as an hypothesis and hypotheses, whether metaphysical or physical, mechanical or those of hidden qualities, should not be taken up in experimental physics. And yet, hypotheses in the hands of Huygens had made possible the founding of this very physics and led him to a truth which the influence of Newton obscured for more than a century and a half—the undulatory theory of light. An hypothesis used as an hypothesis may be most helpful. It is dangerous when it comes to be grasped in the place of a fact itself, since it was only intended to explain facts. It is interesting to note that in spite of his objection to hypotheses Newton could not get away from, or better, could not get along without, the atoms. As to the ether hypothesis, Newton wrote to Boyle: "For my part, I have so little taste for things of this kind that had not your suggestion led me to it I would never, I believe, have put pen to paper about it." He made use of the ether hypothesis in his paper before the Royal Society, entitled "An hypothesis explaining the properties of light" (1675). His theory of gravitation was not regarded by him in the light of an hypothesis. He also made a suggestion as to chemical force, which was not classed by him as an hypothesis, though it seems perilously near one. "I would rather conclude from the holding together of bodies that the particles of the same attract one another with a force which in immediate contact is very great, at a slight distance have as a consequence chemical action, at greater distances exercise no perceptible influence."[1]

At the conclusion of his lecture course before the Royal Institution, Dalton transcribed the following extracts from Newton's "Principia," which, therefore, acquire a double interest: "The parts of all homogenal hard bodies, which fully touch one another, stick together very strongly. And for explaining how this may be some have invented hooked atoms, which is begging the question; and others tell us that bodies are glued together by rest, that is, by relative rest among themselves. I had rather infer from their cohesion that their particles attract one another by some force, which in immediate contact is exceedingly strong, at small distances, performs the chemical operations above mentioned, and reaches not far from the particles with any sensible effort.

"All bodies seem to be composed of hard particles. Even the rays of light seem to be hard bodies, and how such very hard particles which are only laid together and touch only in a few points, can stick together, and that so firmly as they do, without the assistance of something

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[1] Newton: Op. IV. 251.

which causes them to be attracted or pressed towards one another, is very difficult to conceive.

"It seems probable to me that God in the beginning formed matter in solid, massy, hard, impenetrable, movable particles of such sizes and figures and with such other properties, and in such proportion to space as most conduced to the end for which He formed them; and that these primitive particles being solids, are incomparably harder than any porous bodies compounded of them, even so very hard as never to wear or break in pieces, no ordinary power being able to divide what God himself made one in the first creation. While the particles continue entire they may compose bodies of one and the same nature and texture in all ages; but should they wear away or break in pieces, the nature of things depending upon them would be changed. Water and earth, composed of old worn particles and fragments of particles, would not be of the same nature and texture now, with water and earth composed of entire particles in the beginning. And, therefore, that nature may be lasting the changes of corporeal things are to be placed only in the various separations and new associations and motions of these permanent particles, compound bodies being apt to break, not in the midst of solid particles, but where those particles are laid together, and only touch in a few points."

Again, "God is able to create particles of matter of several sizes and figures, and in several proportions to the space they occupy, and perhaps of different densities and forces. At least I see nothing of contradiction in all this."

Again, "Now by the help of these principles all material things seem to have been composed of the hard and solid particles above mentioned, variously associated, in the first creation by the counsel of an intelligent agent."

Boscovich, 1711-1787.

From this time until the close of the 18th century, we find the discussion of atoms largely relegated to the mathematicians, few of them, even, caring to press the investigation of nature along this line. The most important theorizing upon the subject was done by the Italian mathematician and natural philosopher, Boscovich. In his opinion matter was made up of atoms, each atom being an indivisible point, having position in space, capable of motion in a continuous path and possessing certain mass. It was endowed with potential force. Two atoms might attract or repel each other. Two atoms could never coincide, or occupy the same space at the same time. There was no such thing as actual contact between them, all action taking place at a distance. The atom itself possessed no parts or dimensions. In its geometrical aspect it was a mere geometrical point, having no extension in space. Were this alone considered it would be possible for two atoms to exist in the same space but the forces acting between them prevent this.

It may be remarked that such a view of the atom is mathematically logical since this is the only kind of atom which would not be mathematically divisible. The atom of the chemist, having extension in space, must be mathematically divisible. Boscovich's view of the atom as a geometrical point approximates to the modern view of the atom as a center of forces.

It is not necessary to refer here to the views of that other great mathematician, Bernoulli, although they seem to have influenced Dalton and were quoted by him, at least in part. They contained no new contribution to the inquiry we are making.

Neglect of Hypotheses.

Following Newton, we find little concern as to the constitution of matter among the physicists and chemists. The old hypotheses were disregarded or forgotten. Their bearing upon or necessity for the development of natural science was not recognized. The new methods of research and the great impetus given to a practical development of science by better organization opened up fields of such interest and led to discoveries of such moment that far-off theories were laid aside. It is of little interest to follow the treatment of the theories by pure metaphysicians as they could do little to develop them and could contribute nothing to their firm establishment.

It is interesting to note here the reproduction of the condition of affairs which obtained after the period of the flowering of the Greek philosophy. It is as if the race, sated and wearied by a pursuit and refinement of theory far beyond the evidence of facts, had turned for relief to the harvesting of facts without troubling itself about theory. Quite possibly it was not the hypotheses which repelled but the mistaking of hypotheses for facts and their confident assertion as such. "Science warns us," says Huxley, in his "Physical Basis of Life," "that the assertion which outstrips evidence is not only a blunder but a crime." Bishop Berkeley was very careful to draw a distinction here and if chemists accepted his view of the matter that may also serve to explain why they seemed to think hypotheses had little to do with science. He wrote: "What is said of physical forces residing in bodies whether attracting or repelling, is to be regarded only as a mathematical hypothesis and not anything really existing in nature."[1]

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[1] Berkeley: "Siris," p. 234.

CHAPTER III.

The Atomic Theory of Chemistry.

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The conception of atoms had up to the close of the 18th century been almost exclusively the possession of the metaphysician and the mathematical physicist, and had served to develop their sciences. With the exception of Sennert and Boyle, chemists had contributed little to its formulation and less for its establishment, nor had they derived inspiration from it for the proper founding of their own science. For more than a century they had been following the *ignis fatuus* of a false theory of combustion and a most elusive, hypothetical phlogiston. The close of the 18th century found them engaged in bitter strife over these theories, and too fully occupied to think of much else than the wreck of the old beliefs and the adaptation of the new. The master mind of Lavoisier, who had wrought this revolution, was busied with the greater work of reconstruction and, dealing little with hypotheses which could not be directly proved by experiments in his laboratory, was laying broad and strong the foundations of the New Chemistry. And so the works of Bergman, Scheele, Priestley, Black, Cavendish, Macquer and others do not treat of atoms and their moving forces, except in an occasional indefinite reference to some sort of particle.

Yet the chemist was the very one most needed to take this, which had been hitherto really but an atomic hypothesis, and establish it with all the dignity and strength of an atomic theory. Up to this time the facts adduced to substantiate it had been qualitative only. To give it a quantitative basis was reserved for the 19th century and a chemist, and this was the achievement of Dalton. It is scarcely possible to overestimate the service thus rendered or to give him too great credit in connection with the establishment of the atomic theory.

Justice of Dalton's Claim.

The justice of Dalton's claim to the title of founder of the modern atomic theory has been brought into question. The same idea, it has been affirmed, can be discovered in the works of Richter and perhaps others. But this, if true, would only be in accord with the law that knowledge does not come suddenly but is a growth. Glimpses of the light are caught before the full light of day is revealed. The credit belongs to him who voices the unformulated and only partially grasped truth which is in men's minds and clearly states it so as to draw the attention of all men to it. Here and there men had thought out in part the Periodic Law, but Mendeléeff will always be known as its author. To Darwin will always be given the credit of the discovery of the Law of Natural Selection and yet Wells and Mayhew had partly anticipated his Origin of Species by many years, and he gives a list of thirty-five others in the early part of the 19th century who had faintly foreshadowed some of his conclusions. And so it rarely happens that one man discovers and impresses upon his age that which is entirely new and unthought of. If it is too new, and too much ahead of their thinking his audience pays little attention to it and it must wait until the world grows wiser and broader and can assimilate the thought.

Fundamental Laws.

It is a matter of much interest to know what train of thought led Dalton to seek in the atomic theory an explanation of his facts, and this point will be discussed further on, but it is much more important to understand upon what he based the revived hypothesis, founding it so securely that the scientific world was at last induced to accept the hypothesis and accord it the position of the great central theory of science. The three foundation stones made use of by Dalton were the quantitative laws of constant proportions, of interproportionality, and of multiple proportions; three laws that marked the true beginning of the quantitative period in the science of chemistry. The first two of these laws were recognized by those who preceded Dalton, the third he discovered and applied himself. While it is true that the first two had been recognized before, it is also true that the conception of them was confused and the enunciation of them far from distinct before the atomic theory put meaning into them. Besides these quantitative facts, it should be mentioned that the indestructibility of matter, the persistence of the elements and the impossibility of their transmutation were well-recognized principles.

Lavoisier and the New Chemistry.

In tracing the discovery of these quantitative laws it is necessary to have some knowledge of the condition of chemical science at the close of the 18th century. First and most important for our purposes was the introduction of a new definition for the word element which enabled chemists to divide all bodies in nature into simple, undecomposable bodies called elements, and compound bodies made up of those elements. Every substance which could not be decomposed was regarded as an element. The list of these simple bodies speedily became a lengthy one and replaced the short one of the vague essences, or elements, of the Greeks and the alchemists. The metals which had formerly been considered compounds containing the hypothetical phlogiston were now recognized as simple and their calces were known as their compounds with oxygen. In these and other compounds, chemists were busy determining the relations by weight of the constituents. Many of these analyses were carried out with the greatest care by the supporters of the phlogiston theory in defense of their beliefs. As Kopp remarks,[1] it is not reasonable to suppose that men like Bergman, Macquer, Scheele, Cavendish and others would have taken the trouble to make these analyses if they had not believed in the constancy of proportions of the constituents they were determining, but there is no proof that they reversed the thought and considered only such as showed constancy of proportions to be chemical compounds. This thought seems to have been first grasped by Lavoisier. That he did grasp it is quite apparent from his "Traité de Chimie." The different bodies, as for instance the different acids, are spoken of as having definite compositions which can be determined and which serve to distinguish them. While he wrote at first of the existence of an indefinite number of nitric acids, from the colorless to the fuming and deepest colored, a few years later he taught that there were three steps in the combination of nitrogen with oxygen, nitric oxide, nitrous acid, and nitric acid and that the other apparently different acids consisted of nitric acid with more or less nitric oxide absorbed in it. And yet he did not expressly state his belief in the constancy of proportions nor lay it down as one of the doctrines of the science. Gradually the importance of this among the doctrines of chemistry came to be recognized, and where it had been tacitly accepted by many, Proust stated categorically his belief that definite chemical compounds contained fixed and constant proportions of their constituents and supported

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[1] Kopp: "Entwickelung der Chemie," p. 221.

his views by much excellent analytical work. This statement was brought out by the contention of Berthollet that the proportions were not fixed but could be indefinitely varied. His views he embodied in his famous "Essai d'un Statique Chimique." The discussion between these two was not ended until after Dalton's announcement of the atomic theory. The constancy of proportions was then generally accepted.

Law of Interproportionality.

The idea of proportionality in the combining amounts was a matter of slow growth through the 18th century. It was difficult to detect any regularity or deduce any reliable generalization or law because analytical methods were imperfect and the analyses so faulty as to be misleading. Without referring to the few scattered observations which appeared previously, the first work of import in this line was that of Bergman (1775) followed by Wenzel and Kirwan. The chief effort was to determine the amount of acid and base respectively necessary for the production of a neutral salt and from that the relative amounts of different acids requisite for the neutralization of any one base, or the relative amounts of the different bases for one acid. Bergman bases upon his analysis his doctrine of affinity, believing that a base demanded more acid for its neutralization the greater its affinity for the acid. These views were vigorously combatted by Berthollet. Cavendish in 1767 used the term "equivalent" to express the amount of soda or potash which corresponded with a definite amount of lime necessary for the neutralization of a fixed quantity of acid.

Wenzel.

The most careful and accurate analytical work on this subject was done by Wenzel. He published, in 1777, his "Lehre von der Verwandtschaft der Körper." Although he did very excellent work in this, which was utilized by Richter and others afterwards, he failed to note the crucial fact, namely, the persistency of the neutrality in the double decomposition of the neutral salts and so could not discover the generalization which was to be deduced from this. On the contrary, he admitted that, the quantity of the neutral salts which react upon one another being calculated from their known composition, an excess of one may remain after the reaction. Berzelius was therefore in error in speaking of Wenzel as the discoverer of the law, as has been repeatedly pointed out.[1]

Richter. It is to J. B. Richter (1762–1807) that the credit of discovering the law of interproportionality is really to be given, yet this fact was not recognized until after the announcement of the atomic theory and his work received at first but little recognition. This was doubtless in part due to erroneous ideas which he advanced along with the true. Richter's earliest work, his inaugural dissertation, showed the trend of his mind toward the application of mathematics to chemistry. In 1792 he published his important work on stoichiometry ("Anfangsgründe der Stoichiometrie, oder Messkunst chem. Elemente"). In this it is very apparent that he strove to establish numerical generalizations as to the combining properties of acids and bases. He recognized the permanence of neutrality in the double decomposition of two neutral salts which Wenzel had missed but which was also recognized by others after Wenzel had published his treatise. From the permanence of neutrality he drew the deduction that there must be a definite relation between the masses of each neutral compound and that the terms of this relation are of such a nature that they can

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[1] Kopp: "Entwickelung d. Chemie," p. 251.

be determined from the masses of the neutral compounds. Thus there is a proportionality between the quantities of acids uniting with a given weight of base and between the quantities of bases uniting with a given weight of acid. But Richter went further and stated that these quantities form a progression, the terms of which bear to each other a simple ratio, a statement which is not borne out by the facts and which consequently weakened the impression of the former statement.

In 1793 he drew up a table which he called a "Series of Masses."

RICHTER'S SERIES OF MASSES.

	Sulphuric acid.	Muriatic acid.	Nitric acid.
Potash	1.606	2.239	1.143
Soda	1.218	1.699	0.867
Volatile alkali	0.638	0.889	0.453
Baryta	2.224	3.099	1.581
Lime	0.796	1.107	0.565
Magnesia	0.616	0.858	0.438
Alumina	0.526	0.734	0.374

He showed how this table might be utilized to calculate the amounts of acid necessary to neutralize known amounts of bases and *vice versa*. As Wurtz observes[1] the forms of expression used by him are not clear. The thought which he wished to convey can be grasped in the light of later knowledge, but his unfortunate choice of terms and complicated statements must have contributed to the neglect with which his observations were treated. Unquestionably he was a man of rare penetration, but it is equally beyond doubt that it would be most unjust to credit him with having anticipated, in the truest sense, the discovery of Dalton. When one considers that Richter was still an adherent of the phlogistic doctrines and en-

[1] Wurtz : "Atomic Theory," p. 16.

deavored to reconcile his sharp and true insight into the nature of metallic oxides (in which work too, he extended his observation upon neutral salts and showed that the same definiteness of proportion and interproportionality was to be observed in these metallic oxides as in the neutral salts), with this discredited theory, the appropriateness of Wurtz's designation of him as the "profound but perplexed author of the law of interproportionality" must be acknowledged.

Richter was much indebted to G. E. Fischer for the recognition of his work. In 1802, Fischer endeavored to explain and simplify his deductions and succeeded in making the regularities much clearer, and thus aided in demonstrating the law of proportionality. Through Fischer the attention of Berthollet was drawn to Richter's work, and he expressed this opinion as to its value: "The preceding observations seem to me necessarily to lead to the conclusion that in my researches I have only hinted at the laws of affinity, but that Richter has positively established the fact that the different acids follow proportions corresponding with the different alkaline bases in order to produce neutrality. This fact may be of the greatest utility in verifying the experiments which have been made upon the proportions of the elements of salts, and even to determine those which have not yet been decided by experiment, and so furnish the surest and easiest method of accomplishing this object, so important to chemistry."[1]

Fischer reduced the various series given by Richter to one, by giving the ratio which the quantities of acids and bases contained in the series bore to one number, namely, to 1000 parts of sulphuric acid. This greatly simplified it, and, as Wurtz remarks, is the first table of chemical equivalents.

[1] Wurtz: "Atomic Theory," p. 21.

FISCHER'S TABLE.

Alumina	525	Fluoric acid	427
Magnesia	415	Carbonic acid	577
Ammonia	572	Sebacic acid	706
Lime	793	Muriatic acid	712
Soda	859	Oxalic acid	755
Strontia	1329	Phosphoric acid	979
Potash	1605	Formic acid	988
Baryta	2222	Sulphuric acid	1000
Succinic acid	1209	Nitric acid	1405
Acetic acid	1480	Citric acid	1583
		Tartaric acid	1694

In order to prepare a neutral salt, the requisite base and acid must be taken in the proportion of the equivalents given. It may be added that Richter had gone a step beyond this and had observed that the amounts of different metals which combine with a given weight of acid will also combine with a given weight of oxygen. It is important as bearing upon the claims of Dalton that but little attention was given to the work of Richter until eight or nine years after it appeared. Dalton states that he was ignorant of it until some time after his discovery, and Richter himself complains in 1795 that his work was looked upon by chemists as a fruitless speculation.

Law of Multiple Proportion.

The next step from the recognition of equivalents or proportionate numbers was to multiple proportions, but to take that step required a clearer conception of the meaning of the proportionate numbers than was held by the chemists of the time. While several chemists seem to have been so near its discovery as only to have needed the enunciation of it, they failed to realize it and to state the generalization. In fact it was not stated until after the conception of the atomic theory came to Dalton, and it was used by him as one of the facts which most clearly pointed to the existence of atoms as its true explanation.

It had for some years been recognized that two or more compounds could be formed by the same elements. Lavoisier spoke of the compounds of nitrogen and oxygen as the two steps of saturation. Proust, in his discussion with Berthollet, had proved that such compounds were definite in composition and that the proportions differed by leaps, as it were, and not by continuous change. Richter had shown that iron and mercury could combine with oxygen in several proportions so as to form several oxides. Furthermore, it was already customary to state the composition of compounds which contained the same elements in different proportions by giving one element in a fixed proportion and varying the proportions of the second element. This being the case it would seem at first sight impossible to fail to detect the simple ratio existing between the latter proportions, but the truth is, the analyses were too faulty to show this relation. Thus Proust, one of the most careful and accurate chemists of his day, stated that 100 parts of copper combined with 17⅔ to 18 parts of oxygen to form the red oxide and with 25 parts to form the black oxide. The correct numbers are respectively 12.6 and 25.2. Richter came nearer to the discovery of the law than any other for he really tried to derive numerical relations between the different amounts of oxygen combined with the same metal but failed to prove the existence of such, most probably because of the same imperfect data. It remained therefore for Dalton to discover this law and not the least of his achievements is that he divined the law by some sort of intuition in spite of faulty numbers and experiments. His method of reaching his discovery will be discussed later in connection with his atomic theory.

W. Higgins.

Some have maintained that Higgins,[1] who published in 1790 a work dealing with the conflict between the phlogistic and antiphlogistic doctrines, anticipated Dalton in the discovery of multiple proportions and the combination by atoms. An examination of so much of his work as bears upon this question will show that there is too much of error in the conclusions of Higgins to justify the claims made for him. There are some scattered allusions and phrases which might be interpreted as glimpses of the theory. It is stated that in certain compounds the smallest particles of the elements are contained in simple numerical relations and, where there are several compounds of the same two elements, ratios of composition are accepted which correspond with the law of multiple proportions. Thus Higgins assumed that in sulphurous acid 1 part by weight, in sulphuric acid 2 parts by weight of oxygen, to 1 part by weight of sulphur, were to be found. If then the smallest particles of oxygen and sulphur had the same weight there were in the two bodies respectively 1 and 2 smallest particles of oxygen comcombined with 1 of sulphur. So too in nitric oxide, he maintained there were 2 particles of oxygen to 1 of nitrogen and hence 2 smallest particles of oxygen to 1 of nitrogen. In nitric acid there were 5 particles of oxygen to 1 of nitrogen and this he believed to be the maximum possible amount of oxygen which the 1 particle of nitrogen could take up. It cannot be maintained that Higgins always regarded the particles of the elements as having the same weight, for in case of water he assumed 1 particle of hydrogen and 1 particle of oxygen to be present though the weights of the two in the compound were

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[1] "A Comparative View of the Phlogistic and Antiphlogistic Theories, with Inductions, &c.," 1789.

known to be far from equal. Whatever Higgins may have thought of his principle he nowhere states it as a general principle but gives a few such instances, as those mentioned, scattered through his book. Hence it was that no chemist in the fifteen years that intervened between the publication of Higgins and that of Dalton seemed to have found in the book the outline even of the atomic theory. After the announcement of Dalton's theory Higgins claimed to have previously developed the same views himself. While he deserved some credit as having caught glimpses of the atomic idea, certainly he can lay no claim to having even aided in the development of the atomic theory. Unfortunately, Higgins' mode of expression was so confused and indistinct that it is not always clear what he meant nor how much he knew. Part of his work may be interpreted as anticipating the discoveries of Gay-Lussac and the theory of Avogadro, and indeed has been so interpreted, were it not for the fact that other portions of the work, contradict such ideas and show that something else must have been his meaning. His views as to atoms and the constitution of bodies then were confused or not fully matured, and he both failed to recognize their importance and to attempt to draw the attention of chemists to them.

Dalton's Theory.

It is a matter of much interest to trace the steps by which Dalton reached the conclusion that the theory of atoms was the best and most satisfactory explanation of the fundamental facts of chemistry. The laws, whose development we have just followed, seem really to have been unknown to him or to have had little influence upon his thinking. There are extant two accounts of what led up to the discovery. The one is a conversation with Dalton reported by Thomson and the other is one of his own written lectures recently discovered by Roscoe. A third method of getting at the facts is by a critical examination of his published papers at the period of his discovery. These three sources of information it will be well for us to examine and compare at some length.

Thomson's Account.

Thomson's account is as follows[1]: "In the year 1804, on the 26th of August, I spent a day or two at Manchester and was much with Mr. Dalton. At that time he explained to me his notions respecting the composition of bodies. I wrote down at the time the opinions which he offered, and the following account is taken literally from my journal of that date: 'The ultimate particles of all bodies are atoms incapable of further division. These atoms (at least viewed along with their atmosphere of heat) are all spheres and are each of them possessed of particular weights which may be denoted by numbers. For the greater clearness he represented the atoms of the simple bodies by symbols. It was this happy idea of representing the atoms and constitution of bodies by symbols that gave Mr. Dalton's opinions so much clearness. I was delighted with the new light which immediately struck my mind and saw at a glance the immense importance of such a theory when developed. Mr. Dalton informed me that the atomic theory first occurred to him during his investigations of olefiant gas and carburetted hydrogen gases, at that time imperfectly understood, and the composition of which was first developed by Mr. Dalton himself. It was obvious from the experiments which he performed upon them that the constituents of both were carbon and hydrogen and nothing else. He found, fur-

[1] Thomson: "History of Chemistry," II, 289-291.

ther, that if we reckon the carbon in each the same, then carburetted hydrogen gas contains exactly twice as much hydrogen as olefiant gas does. This determined him to state the ratios of these constituents in numbers and to consider the olefiant gas as a compound of 1 atom of carbon and 1 atom of hydrogen; and carburetted hydrogen of 1 atom of carbon and 2 atoms of hydrogen. The idea thus conceived was applied to carbonic oxide, water, ammonia, etc., and numbers representing the atomic weights of oxygen, azote, etc., were deduced from the best analytical experiments which chemistry then possessed. Let not the reader suppose that this was an easy task. Chemistry at that time did not possess a single analysis which could be considered as approaching accuracy. A vast number of facts had been ascertained and a fine foundation laid for future investigation, but nothing, as far as weight and measure were concerned, deserving the least confidence existed. We need not be surprised then that Mr. Dalton's first numbers were not exact. It required infinite sagacity and not a little labor to come so near the truth as he did.' "

It is quite clear from this account that Thomson thought the atomic theory resulted from the consideration of the work with the two hydrocarbons, but Dalton's statement is that the idea came to him at the time when he was engaged upon the work, or rather was fully formulated then, and he made use of the example of these hydrocarbons to make it plain to Thomson. This can be shown to be the case both from his own later account and from the consideration of his other published papers.

Dalton's Lecture Notes.

His original lecture notes from which the second account is taken are dated February 3, 1810, and were for a series of lectures delivered before the Royal Institution of London.

" Having been long accustomed to make meteorological observations, and to speculate upon the nature and constitution of the atmosphere, it often struck me with wonder how a compound atmosphere, or a mixture of two or more elastic fluids, should constitute apparently a homogeneous mass, or one in all mechanical relations agreeing with a simple atmosphere."

"Newton had demonstrated clearly in the 23rd proposition of Book 2 of the 'Principia,' that an elastic fluid is constituted of small particles or atoms of matter which repel each other by a force increasing in proportion as their distance diminishes. But modern discoveries have ascertained that the atmosphere contains three or more elastic fluids of different gravities; it did not appear to me how this proposition of Newton would apply to a case of which he, of course, could have no idea.

" The same difficulty occurred to Dr. Priestley, who discovered this compound nature of the atmosphere. He could not conceive why the oxygen gas being specifically heavier, should not form a distinct stratum of air at the bottom of the atmosphere and the azotic gas one at the top of the atmosphere. Some chemists upon the continent, I believe the French, found a solution of this difficulty (as they apprehended). It was chemical affinity. One species of gas was held in solution by the other; and this compound in its turn dissolved water; hence evaporation, rain, etc. This opinion of air dissolving water had long before been the prevailing one, and naturally paved the way for the reception of that which followed, of one kind of air dissolving another. It was objected that there were no decisive marks of chemical union when one kind of air was mixed with another—the answer was that the affinity was of a very slight kind, not of that energetic cast that is observable in most other cases."

Dalton then described at some length his efforts at adapting the "chemical theory of the atmosphere to the Newtonian doctrine of repulsive atoms or particles." He continues: "In 1801 I hit upon an hypothesis which completely obviated the difficulties. According to this we were to suppose that the atoms of one kind did not repel the atoms of another kind but only those of their own kind. This hypothesis most effectually provided for the diffusion of any one gas through another, whatever might be their specific gravities and perfectly reconciled any mixture of gases to the Newtonian theorem. Every atom of both or all of the gases in the mixture was the center of repulsion to the proximate particles of its own kind, disregarding those of the other kind. All the gases united in their efforts in counteracting the pressure of the atmosphere or any other pressure that might be opposed to them. This hypothesis, however beautiful might be its application, had some improbable features.

"We were to suppose as many distinct kinds of repulsive powers as of gases; and moreover, to suppose that heat was not the repulsive power in any one case; positions certainly not very probable. Besides I found from a train of experiments, which have been published in the 'Manchester Memoirs,' that the diffusion of gases through each other was a slow process, and appeared to be a work of considerable effort. Under reconsidering the subject, it occurred to me that I had never contemplated the effect of difference of size in the particles of elastic fluids. By size I mean the hard particles at the center and the atmosphere of heat taken together. If, for instance, there be not exactly the same number of atoms of oxygen in a given volume of air as of azote in the same volume, then the sizes of the particles of oxygen must be different from those of azote. And if the sizes be different, then on the supposition that the repulsive power is heat, no equilibrium can be established by particles of unequal sizes pressing against each other.

"This idea occurred to me in 1805. I soon found that the sizes of the particles of elastic fluids must be different; for a measure of azotic gas and one of oxygen, if chemically united, would make nearly two measures of nitrous gas, and those two could not have more atoms of nitrous gas than the one measure had of azote or oxygen. Hence the suggestion that all gases of different kinds have a difference in the size of their atoms, and thus we arrive at the reason for that diffusion of every gas through every other gas, without calling in any other repulsive power than the well-known one of heat. This then is the present view which I have of the constitution of a mixture of elastic fluids. The different sizes of the particles of elastic fluids under like circumstance of temperature and pressure being once established, it became an object to determine the relative sizes and weights, together with the relative number of atoms in a given volume. This led the way to the combination of gases and to the number of atoms entering into such combinations, the particulars of which will be detailed more at length in the sequel. Other bodies besides elastic fluids, namely, liquids and solids, were subject to investigation in consequence of their combining with elastic fluids. Thus a train of investigation was laid for determining the number and weight of all chemical elementary principles which enter into any sort of combination, one with another."[1]

As Roscoe and Harden remark, it may be well to remember that according to Dalton's view, which is a modi-

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[1] Roscoe and Harden: "New View of Dalton's Atomic Theory," p. 13.

fication of that of Newton and Lavoisier, each atom or particle of a gas consisted of an exceedingly small central nucleus of solid matter surrounded by an enormously more bulky elastic atmosphere of heat, of great density next the atom, but gradually growing rarer according to some power of the distance. To this atmosphere of heat was ascribed the power of repulsion by means of which the elastic state of the gas was maintained. By increasing the amount of heat round each atom the density of the gas would therefore be diminished.[1]

The same authors observe that the date 1805 given above by Dalton must be a clerical error for 1803 since he had communicated an account of the atomic theory to Thomson in 1804 and as can be seen from his note-books had worked out a table of the diameters of the atoms in September, 1803.

Deductions from Other Papers.

To complete the view of the inception of the modern atomic theory it is necessary now to consider the early papers published by Dalton which bear upon this subject. Dalton's training was more especially that of a mathematician and physicist, and he was particularly interested in meteorological observations and the phenomena of gases. In 1793 he published[2] his first researches having for their object the elucidations of certain meteorological points, especially the moisture in the atmosphere and the conditions under which this water vapor existed there. This question seemed to have been one of peculiar fascination and interest for him. Eight years later (1801)[3] he published a paper on the "Constitution of Mixed Gases." In this he asserted that the total pres-

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[1] Roscoe and Harden, p. 19.

[2] "Meteorological Observations and Essays," Manchester, 1793.

[3] Memoirs, Manchester Lit. and Phil. Soc., V, 535.

sure of a mixture of two gases on the walls of the containing vessel is equal to the sum of the pressures of each gas; if one gas is removed, the pressure now exerted by the remaining gas is exactly the same as was exerted by that gas in the original mixture. The variations in the pressure of various gases caused by increasing and decreasing temperature were considered and the relations which exist between the volumes of gases and the temperature at which these volumes were measured. As a mathematician the idea of Bernoulli was probably known to him that the pressure exerted by a gas on the walls of a vessel enclosing it was due to the constant bombardment of the walls by the atoms of which the gas consisted.

Dalton says of this paper, in a second memoir[1] published in 1802: "My principal object in that essay was to point out the manner in which elastic fluids exist together, and to insist upon what I think is a very important and fundamental position in the doctrine of such fluids, namely, that the elastic or repulsive power of each particle is confined to those of its own kind and consequently the force of such fluid, retained in a given vessel, or gravitating, is the same in a separate as in a mixed state, depending upon its proper density and temperature."

Dalton read on November 12, 1802, a paper,[2] entitled "An Experimental Enquiry into the Properties of the Several Gases or Elastic Fluids, Constituting the Atmosphere." He set forth his aim in this research as follows:

1. To determine the weight of each simple atmosphere abstractedly, or, in other words, what part of the weight of the whole compound atmosphere is due to azote; what to oxygen, etc.

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[1] Memoirs Manchester, Lit. and Phil. Society, 1802.

[2] Manchester Memoirs, I, pp. 248, 249.

2. To determine the relative weights of the different gases in a given volume of atmospheric air, such as it is at the earth's surface.

3. To investigate the properties of the gases to each other, such as they ought to be found at different elevations above the earth's surface.

In this memoir he clearly states his belief that the atmosphere was not a chemical compound. In connection with his careful working out of the proportions by weight of the constituents of the atmosphere, it should be remembered that the work of Gay-Lussac and Humboldt upon the analysis of the air was not presented before the French Academy until three years later, in 1805. In another paper at this time Dalton showed that all gases expanded alike from heat, and that this expansion was very nearly 1/480th of the volume for each additional 1° F. In this he again anticipated Gay-Lussac in his classic work upon the same subject. While Dalton's main results in these investigations have apparently little direct bearing upon the subject under discussion, they are briefly mentioned here to show the trend of his work and thoughts. But there is one portion of his "Enquiry into the Properties of Elastic Fluids" which has a very direct bearing upon the subject, giving the first glimpse of the law of multiple proportions. In determining the amount of oxygen in the atmosphere, the following experiment was performed:

"If 100 measures of common air be put to 36 of pure nitrous gas in a tube 0.3 inch wide and 5 inches long, after a few minutes the whole will be reduced to 79 or 80 measures and exhibit no signs of either oxygenous or nitrous gas. If 100 measures of common air be admitted to 72 of nitrous gas in a wide vessel over water, such as to form a thin stratum of air, and an immediate momentary agitation be used, there will, as before, be found 79 or 80 measures of pure azotic gas for a residuum.

"If in this last experiment less than 72 measures of nitrous gas be used, there will be a residuum containing oxygenous gas; if more, then some residuary, nitrous gas, will be found. These facts clearly point out the theory of the process; the elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity. In the former case, nitric acid is the result, in the latter, nitrous acid."

With regard to this experiment Roscoe says:[1] "In the memorable case in which Dalton announces the first instance of combination in multiple proportions, the whole conclusion is based upon an erroneous experimental basis. If we repeat the experiment, as described by Dalton, we do not obtain the results he arrived at. We see that Dalton's conclusions were correct, although in this case it appears to have been a mere chance that his experimental results rendered such a conclusion possible."

I have seen no suggestions as to what Dalton meant by the "elements of oxygen" in the passage cited above. The word 'elements' seems meaningless unless he was here thinking of the component particles of this gas which he well recognized was not compound. At the same time he knew that nitrous oxide was compound, and so this experiment did not have the simplicity of his next example of multiple proportions in which he was dealing with carbon and hydrogen alone.

First Publication of the Theory by Dalton.

A paper[2] on the "Absorption of Gases by Water and Other Liquids" was read by Dalton, before the Manchester Society on October 21, 1803.

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[1] Roscoe: *Chem. News*, **30**, 266–267.

[2] Manchester Memoirs, 1805.

There are fifteen propositions made in this article; some statements of well-known facts, others the result of experiments performed by Dalton and Henry. Upon these was built a mechanical theory of the absorption of gases. In this discussion there is frequent reference to "particles of gas." Thus, "A particle of gas pressing on the surface of water is analogous to a single shot pressing upon the summit of a square pile of them;" or again, "each particle of gas must divide its force equally amongst a number of particles of water." The article closes with the following noteworthy sentences:

"The greatest difficulty attending the mechanical hypothesis arises from different gases observing different laws. Why does water not admit its bulk of every kind of gas alike? This question I have duly considered and though I am not yet able to satisfy myself completely I am nearly persuaded that the circumstance depends upon the weight and number of the ultimate particles of the several gases; those whose particles are lightest and single being least absorbable, and the others more, according as they increase in weight and complexity (he added in a foot-note: 'Subsequent experiment renders this conjecture less probable'). An inquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new. I have lately been prosecuting this inquiry with remarkable success. The principle cannot be entered upon in this paper, but I shall just subjoin the results, as far as they appear to be ascertained by my experiments."

TABLE OF THE RELATIVE WEIGHTS OF THE ULTIMATE PARTICLES OF GASEOUS AND OTHER BODIES.

Hydrogen	1.0
Azot	4.2
Carbone	4.3

Ammonia	5.2
Oxygen	5.5
Water	6.5
Phosphorus	7.2
Phosphuretted hydrogen	8.2
Nitrous gas	9.3
Ether	9.6
Gaseous oxide of carbone	9.8
Nitrous oxide	13.7
Sulphur	14.4
Nitric acid	15.2
Sulphuretted hydrogen	15.4
Carbonic acid	15.3
Alcohol	15.1
Sulphureous acid	19.9
Sulphuric acid	25.4
Carburetted hydrogen from stagnant water	6.3
Olefiant gas	5.3

First Table of Atomic Weights.

While this and the previous paper bear the date 1802, the volume of the memoirs of the Manchester Literary and Philosophical Society containing them was not published until 1805, and there is good reason for believing that during these three years, in which they lay unpublished, Dalton added to them such new facts and conclusions as occurred to him and seemed necessary to bring them up to date. Roscoe has shown conclusively from the testimony of Dalton's laboratory note-book, that he was still experimenting in 1803 as if he were in ignorance of the remarkable experiment described on page 92 which gave the first recorded case of multiple proportions. This experiment itself is given later in the note-books but unfortunately without date.

And so with regard to the table of weights given above, it may be fairly concluded that this was not the original table but a later corrected one, for Roscoe and Harden[1]

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[1] Roscoe and Harden, p. 28.

have found in the same note-books under date September 6, 1803, or some six weeks before the reading of the paper before the Society, the following table which seems to be the first attempt at a table of the atomic weights.

DALTON'S FIRST ESSAY AT A TABLE OF ATOMIC WEIGHTS, SEPTEMBER 6, 1803.

Ult. at. Hydrogen	1.0
Oxygen	5.66
Azot	4.0
Carbon (charcoal)	4.5
Water	6.66
Ammonia	5.0
Nitrous gas	9.66
Nitrous oxide	13.66
Nitric acid	15.32
Sulphur	17.00
Sulphureous acid	22.66
Sulphuric acid	28.32
Carbonic acid	15.8
Oxide of carbone	10.2

There is no evidence from the note-books of the construction of the other table at or near the time given at the heading of the paper. Dalton was secretary of the Society and of course had abundant opportunity to insert such changes as he saw fit. There could have been no question in his mind as to priority or historical claims, his aim being simply scientific accuracy.

The table is worthy of careful study. The mention of "ultimate atoms" is found here and elsewhere in these note-books of the same date. Dalton's theory was at first evidently corpuscular like that of Newton. His atom was not an indivisible unit but a particle or little mass. It grew into an atomic theory with greater knowledge. Again, we have here three distinct cases of multiple proportions and yet there is no reference to the case of olefiant gas and carburetted hydrogen which, from the conversation with Thomson, was the first or at least the deciding case which led him both to the law of multiple proportions and the atomic theory.

Inception of the Theory.

It is clear from all that has been said that Dalton's taking up of the atomic theory was no sudden inspiration springing from some newly acquired fact, but a matter of slow growth, coming first from his meteorological and mathematical studies and in particular from his thinking over the problem connected with the gases of the atmosphere; and that he thought long and deeply over these problems, declining to accept the usual explanations and gradually substituting the corpuscular theory. His chemical experiments enabled him to very wonderfully substantiate this theory, but the accepted theory of elements made it necessary to convert the corpuscular into an atomic theory. It is doubtful whether Dalton thought out or cared about the difference between the two ideas, for, after all, his theory was at the beginning very simple and crude. It seems to be impossible to fix upon any exact date for the inception of the atomic theory, but the date most worthy of being so accepted would be the one given in his note-book along with the first table of atomic weights, namely, September 6, 1803. Henry[1] sums up the evidence known to him as follows: "My own belief is that during the three years (1802–1804) in which the main foundations of the atomic theory were laid, Dalton had patiently and maturely reflected on all the phenomena of chemical combination known to him from his own researches or those of others, and had grasped in his comprehensive survey, as significant to him of a deeper meaning than to his predecessors, their empirical laws of constant and reciprocal propor-

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[1] Henry: "Life of Dalton," p. 85.

tions, and his own researches in the chemistry of aeriform bodies." Henry adds that after the lapse of twenty years Dalton himself may have failed in recalling the antecedents of his great discovery in the exact order of sequence. If individual judgment has any more value in such a matter than a mere guess, it might be suggested that the account in his lecture of 1810 is the result of the mature and deliberate sifting of the earlier thoughts and beliefs, whereas in the conversation of 1804, with a desire for bringing about conviction in his hearer, he gave as the foundation of his theory the facts which had been most recently acquired and so most impressed him and offered the best means of making his meaning clear.

Thomson's evidence is direct and conclusive as to Dalton's independence of the previous work of Richter. He says: "I do not know when he adopted these notions (*i. e.*, the atomic theory), but when I visited him in 1804 at Manchester he had adopted them, and at that time both Mr. Dalton himself and myself were ignorant of what had been done by Richter on the same subject."[1]

Conclusions of Roscoe and Harden.

This discussion may well be concluded with the remarks of Roscoe and Harden:[2] "There seems to be no doubt that the idea of atomic structure arose in Dalton's mind as a purely physical conception, forced upon him by his study of the physical properties of the atmosphere and other gases. Confronted in the course of this study with the problem of ascertaining the relative diameters of the particles, of which he was firmly convinced all gases were made up, he had recourse to the results of chemical analysis. Assisted by the assumption that combination always takes place in the simplest pos-

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[1] Proc. Glasgow Phil. Soc., 1845-46, p. 86.

[2] Roscoe and Harden: "New View of Dalton's Atomic Theory," p. 50.

sible way, he thus arrived at the idea that chemical combination takes place between particles of different weights, and this it was which differentiated his theory from the historic speculations of the Greeks. The extension of this idea to substances in general led him to the law of combination in multiple proportions, and the comparison with experiment brilliantly confirmed the truth of his deduction. Once discovered, the principle of atomic union was found to be of universal application. Nothing essential has since been added to our knowledge of the laws of chemical combination by weight. To Dalton must be ascribed the rare merit of having by the application of a single felicitous idea to a whole class of the facts of chemistry, so completely comprehended the prevailing relations that his generalizations have sustained without alteration the labors and changes of almost an entire century.

Details of Dalton's Theory.

The details of Dalton's atomic theory were very few and simple. He did not concern himself with the vexed questions concerning these atoms with which the centuries struggled. The following statements may be gathered from his "New System of Chemical Philosophy."

1. All bodies of sensible magnitude are constituted of a vast number of extremely small particles or atoms of matter bound together by a force of attraction which, as it endeavors to prevent their separation, is called attraction of cohesion; but as it collects them from a dispersed state is called attraction of aggregation or more simply affinity.[1]

2. The ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc. In other words

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[1] Dalton's "System of Chemical Philosophy," p. 143.

every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen; etc.[1]

3. No new creation or destruction of matter is within the reach of chemical agency. All the elements we can produce consist in separating particles that are in a state of cohesion or combination and joining those that were previously at a distance.[2]

4. The ultimate particles of all simple bodies are atoms incapable of further division. These atoms (at least viewed along with their atmospheres of heat) are all spheres and are possessed of particular weights which may be denoted by number.[3]

5. If there are two bodies which are disposed to combine, then their combination takes place by atoms.[4]

6. In an elastic gas each particle occupies the center of a comparatively large sphere and supports its dignity by keeping all the rest, which by their gravity or otherwise are disposed to encroach upon it, at a respectful distance.[5]

It will be observed that such questions as the existence of vacua, filling of space, inherent motion of the particles, etc., are left without mention. And it was well for the atomic theory to begin life again clothed with as few of these debatable notions as possible. The simplicity of Dalton's statement is therefore praiseworthy. It is scarcely necessary to call attention to its crudities.

Reception of the Theory.

Dalton's papers read before the Manchester Society seem to have attracted but little attention. They really con-

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[1] Dalton's "New System," p. 141.

[2] Dalton's "New System," p. 212.

[3] Thomson's "History of Chem.," p. 289.

[4] Dalton's "New System," p. 216.

[5] Dalton's "New System," p. 211.

tained no clear definite announcement of the atomic theory and in the main were filled with other matters. It is only in the light of later events that we can pick out here and there from the earlier papers sentences presaging the coming theory. And these papers did not reach the larger circle of scientific readers outside as they were not published for some years after they were read before the society. It was mainly through Thomson that Dalton's conclusions were made known to chemists. He gave a sketch of the theory in his "System of Chemistry," published in 1807. In the same year he published in the *Philosophical Transactions* a paper giving an example of multiple proportions. This paper was on oxalic acid and in it Thomson showed that oxalic acid united in two proportions with strontium and that, supposing the strontium in both salts to be represented by the same amount, then the oxalic acid in one is twice as much as in the other.

A few months later, Wollaston read before the Royal Society of London a paper upon peracid and subacid salts in which he showed how the law of multiples was further exemplified in the alkaline carbonates and bicarbonates, potassium sulphate and bisulphate, and potassium oxalates. To this article Wollaston appended some noteworthy observations upon the arrangement of atoms in space which will be referred to later. These publications gradually drew the attention of chemists to Dalton's views. Some of the most eminent chemists, however, were very hostile to the theory. Sir Humphry Davy was particularly opposed to it and even descended to caricaturing and ridiculing it. But Wollaston and Thomson and Gilbert were won over and the latter convinced Davy so that he too became a strenuous supporter of the theory.

Extension of the Theory by Berzelius.

The chemist who did most for the extension of the law of multiple proportions, the determination of atomic weights and the development of the theory, was Berzelius. From 1810 on, its acceptance became general among chemists. It was in his "New System of Chemical Philosophy," in 1808, that Dalton first gathered together his views as to the atoms. They were placed under the heading "Chemical Synthesis" and formed the third portion of the book, though occupying altogether only a few pages. In this he does not give facts upon which he based the theory but simply expresses his conclusions. He introduced his symbols which were somewhat cumbrous and were afterwards replaced by the symbols of Berzelius which are practically those at present in use. Dalton's introduction of symbols was a most important advance and rendered his theory much clearer. He appended a table giving the symbols and atomic weights of 37 bodies, 20 of which were then considered simple. A few of these are given here to show the general character of his numbers.

Hydrogen	1	Phosphorus	9
Azote	5	Sulphur	13
Carbon	5	Iron	38
Oxygen	7	Copper	56, etc.

He chose hydrogen as the standard because it was the lightest of all bodies. He thought all the atomic weights of other bodies to be most probably multiples of hydrogen and so expressed them by whole numbers.

In 1810 the second volume of Dalton's "New System of Chemical Philosophy" appeared. It was mainly concerned with ingenious efforts at determining the atomic weights and he gave a new table of these weights, fuller than the preceding one but still very faulty.

The third volume did not appear until 1827. It contained a new table of atomic weights and in it he still adhered to his ratio of 1 : 7 for hydrogen and oxygen, refusing to accept the more accurate results of other chemists.

Dalton's Rules for Determining the Atomic Weights.

Dalton had recognized that the first task facing chemists in the light of the new theory was the determination of the relative weights of the atoms. This was to be accomplished by correct analyses of well-characterized compounds which gave the most direct ratios. He made use not only of his own analyses but of the best work of others known to him. One of the most serious problems connected with this work was that of determining the number of atoms in the various compounds. For this purpose Dalton laid down a number of arbitrary rules, proceeding upon the assumption that nature always worked in the simplest, most direct manner, an assumption which is far from justifiable in the sense accepted by Dalton. His rules were as follows :

1. When only one combination of two bodies can be obtained, it must be presumed to be a binary one, unless some cause appear to the contrary.

2. When two combinations are observed, they must be presumed to be a binary and a ternary.

3. When three combinations are obtained, we may expect one to be binary and the other two ternary.

4. When four combinations are observed, we should expect one binary, two ternary and one quaternary.

A binary compound meant one of 2 atoms, ternary of 3 atoms, quaternary of 4 atoms, etc.

He also adopted as a principle the theory that the atomic weights were all multiplies of hydrogen and therefore whole numbers. Consequently in his later tables, all fractions were rounded off to the nearest integers. His numbers were very faulty and after 1810 found little acceptance.

Far better work was done by Berzelius, though he also found it necessary to adopt arbitrary rules for telling the number of atoms in a given compound. His rules may be briefly stated thus: Summing up all of his experiments and investigations he believed that the following rules could be deduced:

If an element forms several oxides, and the quantities of oxygen contained in them, as compared with a fixed quantity of the element, are to each other as 1:2, then it is to be concluded that the first compound consists of 1 atom of the element and 1 atom of oxygen; the second of 1 atom of the element and 2 atoms of oxygen (or 2 atoms of the element and 4 atoms of oxygen). If the ratio is 2:3, then the first compound consists of 1 atom of the element and 2 atoms of oxygen; the second of 1 atom of the element and 3 atoms of oxygen, etc.

Bring Disfavor.

Something more was needed, however, than mere arbitrary rules. In fact, the atomic theory itself being an assumption, further steps in its development and utilization should so far as possible be based on facts and not on other assumptions. Such arbitrary measures as those just described left the whole matter in the position of 'an hypothesis bristling with other hypotheses.' Another inconsistency of Dalton, which brought his entire theory into question once more, lay in his use of the word atom. This term covered both simple particles and compound, the divisible and the indivisible. It was thoroughly illogical and speedily led into difficulties. It was doubtless this confusion of ideas which led Dalton to reject the relations of gaseous volumes discovered by Gay-Lussac.

Terms Substituted for Atoms.

To avoid these difficulties and inconsistencies, Davy first suggested the use of the word 'proportions' instead of atomic weights. Wollaston preferred the term 'equivalents,' formerly used by Cavendish, and a great many followed his lead. In his table of 1814, Wollaston gave the combining weights of elements and compounds together, calling all equivalents and declining to consider them atomic weights.

The term 'equivalent' strictly means the weight of an element found by analysis of compounds which is equivalent to the unit weight of the standard element and will combine with it or with equivalents of other elements. It differed in the minds of Wollaston and those who followed him from the term atom in that there was no effort whatever at settling the number of supposed atoms in the compound but the weights were taken as found in the analysis. Of course, if the number of particles in the compound be considered, then the term equivalent becomes identical with atomic weight, and unless they are considered one has in many cases the choice between several possible equivalents. If there had only been a few compounds to deal with the matter would have been comparatively simple but the number was very large and was being continually added to, so perplexity in the matter of choice was correspondingly great.

For more than half a century afterwards, these terms 'combining weights,' 'proportions,' and 'equivalents' were used by many very conservative chemists in preference to the term 'atomic weight'. Of course this substitution practically abandoned the idea of atoms and, in theory, was but little in advance of the position held by Richter and others.

Thomson says with regard to this:[1] "But in fact these terms 'proportion,' 'equivalent' are neither of them so convenient as the term atom; and unless we adopt the hypothesis with which Dalton set out, namely, that the ultimate particles of bodies are atoms incapable of further division, and that chemical combination consists in the union of these atoms with each other, we lose all the new light which the atomic theory throws upon chemistry and bring our notions back to the obscurity of the days of Bergman and of Berthollet."

Combining Volumes.

With the discoveries of Gay-Lussac, another mode of determining these combining numbers was put into practice, and that was by a consideration of the combining gaseous volumes. Not all of the elementary numbers could be determined in this way, still there arose a "theory of volumes" in which the effort was made to extend the idea theoretically to all elements. Thus they spoke of elementary volumes of carbon and other solid elements. In deducing the elementary volume of carbon, for example, the formation of carbon dioxide was considered. Here two volumes of oxygen are required for the formation of two volumes of carbon dioxide. Now do these contain one volume of carbon or two volumes of carbon? Berzelius decided from analogy to the condensation in the case of water that there was one volume of carbon. And so we see that here, too, the old difficulty appeared and had to be met by a selective use of analysis and hypothesis and was full of uncertainties. And yet many accepted this hypothesis,

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[1] Thomson: "History of Chemistry," II., p. 294.

especially among the French chemists, and sought to substitute the word "volumes" for atoms, thinking that this was more in accordance with the facts and depended less upon speculative hypotheses. But after all, this, like the others, was nothing more than a change of terms. In 1818, Berzelius endeavored, by formulating what he called a corpuscular theory, to reconcile the atomic theory of Dalton where the fixed proportions were determined by weight, and the elementary volume theory, where they were found by the combination of gaseous volumes. He spoke of indivisible corpuscles, ultimate particles, chemical equivalents, combining proportions, and molecules as synonymous with atoms. It is needless to say that there could only be confusion of ideas where such confusion of terms existed. He observed that the atomic theory, theory of volumes and corpuscular theory led to about the same results. He came to the conclusion that equal volumes of gases contained equal numbers of atoms, but that this did not apply to compound gases. This was an unfortunate divergence, as will be seen, from the theory of Avogadro which was at that time practically ignored, at least in its original form. Proust also, as Berzelius points out, made use of the volume theory.

Confusion and Division.

Thus, a dozen years after the announcement of the atomic theory we find great confusion and division of opinion; Dalton and Gay-Lussac would not accept the views of Berzelius; Wollaston rejected atoms for equivalents; Davy for proportional numbers; the French chemists for elementary volumes; all with the idea that they were eschewing theory and confining themselves strictly to facts. Misconception and confusion were in a fair way, as Wurtz has said, of rendering sterile Dalton's profound conception and consigning it to oblivion.

CHAPTER IV.

The Relative Weights of the Atoms.

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THE RELATIVE WEIGHTS OF THE ATOMS.

The first and most important development of the atomic theory centers around the determination of the number of atoms in the molecule. This problem, as has been seen, formed a serious obstacle in the path of chemists from the very beginning of the application of the atomic theory and threatened to wreck the entire theory, though such a conclusion was both unnecessary and illogical. The empirical rules of Dalton and especially of Berzelius, whose experience was much wider and analytical skill much greater, gave very fair results but there was no means of testing the accuracy attained and, if empiricism was to be the guide, many scientific men preferred pure empiricism unmixed with theory.

Gaseous Molecules, Law of Pressures.

The easiest line of attack of this problem lay in the study of the gaseous molecules and the first generalization in this direction was the theory of Avogadro, sometimes called the Law of Avogadro. This theory was based upon and offered in explanation of three observed laws. First there was Boyle's law as to the effect of pressure upon volumes of gases. Equal volumes of gases were found by Boyle to suffer the same decrease in volume when subjected to equal pressures and this was independent of the nature of the gas. The volume of a gas was then inversely proportional to the pressure if the temperature remained the same. Mariotte reached the same conclusion independently of Boyle some seventeen years later. This law, announced in the 17th century, has been subjected to very careful testing in the

19th century. In 1825 Despretz showed that the law was not rigorously exact. It is a very close approximation to the truth, however, except for gases near their points of liquefaction. Later experiments of Regnault show that Boyle's law is not even true for the more difficultly liquefiable gases. It would seem that there is a temperature at which the compressibility is exactly represented by Boyle's law. These facts were unknown at the time Avogadro announced his theory (1811), the law being then regarded as rigorously exact.

Law of Temperatures.

It has already been stated that some of Dalton's earliest work was upon the effect of temperature upon the volumes of various gases. In this he anticipated Gay-Lussac. The result of the work of these two investigators was the establishment of the law of temperatures, namely, that all gases expand alike for the same increase of temperature. Hence, under constant pressure the volumes of gases are directly proportional to the temperature. The coefficient of expansion is independent of the pressure, and is now known to be $\frac{1}{273}$ of the volume at 0° for every 1° centigrade between 0° and 100°. This law, like the previous one, was for some time held to be strictly true. That it is subject to the same modifications as the law of pressures, has been shown by the experiments of Pouillet, Rydberg, Magnus and Regnault. The coefficient of expansion is sensibly affected by the pressure, especially when gases near their points of liquefaction, and this coefficient varies slightly for various gases, so that it may be said that each gas has its own coefficient of expansion by heat as it has its coefficient of compressibility. In the case of air, hydrogen and the more permanent gases, these coefficients approximate very closely to one another.

Law of Volumes.

The third law is that called the law of volumes, and it was chiefly in explanation of this that Avogadro offered his theory. This law is generally accredited to Gay-Lussac, and rightly so, as it was established mainly through his work. At the beginning of the 19th century, Gay-Lussac was at work upon the combination of gases by volumes. In 1805, working conjointly with Humboldt,[1] he found that 1 volume of oxygen and 2 volumes of hydrogen combined to form water. They were struck by the exactness of these proportions, and further, that they held good for any temperature. Gay-Lussac extended the investigation to various other gases, and in 1808 stated his results before the Société Philomathique in Paris. Briefly summed up, the law of Gay-Lussac is that the volumes of combining gases bear a simple relation to each other, and secondly that there is also a simple ratio between the volumes of the gaseous product and of the combining constituents. In stating his discovery Gay-Lussac recalled the discussion of Proust and Berthollet over the law of definite proportions and the doctrine of Dalton that substances combine by simple atoms, evidently holding some such theory as the explanation of his law.

So many examples were brought forward by Gay-Lussac in which the simple ratio of the combining volumes was observable that the generalization was soon accepted. A few instances, for purposes of illustration may be mentioned here:

1	vol.	nitrogen	and	1	vol.	oxygen	give	2	vol.	nitrogen dioxide.
1	“	chlorine	“	1	“	hydrogen	“	2	“	hydrochloric acid.
2	“	hydrogen	“	1	“	oxygen	“	2	“	water.
2	“	nitrogen	“	1	“	oxygen	“	2	“	nitrogen monoxide.
1	“	nitrogen	“	3	“	hydrogen	“	2	“	ammonia.
1	“	ethylene	“	1	“	chlorine	“	1	“	ethylene chloride.

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[1] *Jour. de Physique*, **60**, 129.

Opposition of Dalton.

In the second part of his "New System of Chemistry" appearing in 1810, Dalton spoke of the conclusions of Gay-Lussac as erroneous. This was a strange position, as Kopp remarks,[1] for one to take with regard to regularity in combination by volume who had maintained the existence of a similar regularity in composition by weight. Dalton stated that, if it were true that gases combined by volumes and in so simple a relation as 1 with 1, or 2, or 3, then this would chime in well with his theory of atoms. It was clear, however, that it could only be true if equal volumes of gases contained either the same number of atoms or such numbers as stand in a simple ratio to one another. He then strove to show that Gay-Lussac's generalization was not supported by the facts. According to his belief the combination was never exactly by equal volumes. The nearest approach to such a regularity was to be seen in the combination of oxygen and hydrogen to form water, but even here, according to his most trusted experiments, it was one volume of oxygen combining with 1.97 volumes of hydrogen. He had in former years held that the atoms of all gaseous bodies had the same volume and that in equal volumes of oxygen and hydrogen there were equal numbers of atoms, but on further consideration he had come to the conclusion that the atoms of different gases were not equally large.

Dalton's objections did not prevent the general acceptance of Gay-Lussac's law. Careful workers speedily recognized its correctness within the limits of experimental error, and that it was not an hypothesis, as Dalton had called it, but a generalization which could be shown to be true.

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[1] "Entwick. d. Chem.," p. 340.

Law of Densities.

In spite of Dalton's views, this fact of the combination of gases by simple volume gave strong support to the atomic theory. It fell into line with the observation of the fixed relation by weight of the combining bodies, and the multiple weight relations are encountered again in the combination by volumes. If this law of volumes is true then there should exist a simple relation also between the specific gravities of elementary gases and their atomic weights. This was seen by Gay-Lussac and clearly shown and defined by Berzelius, but Dalton refused to accept it and ignored this also. There was some force in Dalton's objection. The relation between the atomic weights and specific gravities was not so simple as had seemed at first sight, though for quite a while it was held to be simple. It has required half a century to remove all of the difficulties. The following table gives the relations for some of the elements. In this table the numbers in the second column represent the densities (*d*), or specific gravities of the elements in the form of gas, in the third column are the atomic weights (*w*), and in the fourth column the ratios (*w*/*d*) between the atomic weights and the densities.

Element.	*d.* Density.	*w.* At. wt.	*w*/*d*.
Hydrogen	0.0692	1.0	14.45
Chlorine	2.440	35.4	14.51
Bromine	5.54	79.9	14.42
Iodine	8.716	126.5	14.51
Oxygen	1.10563	8.0	7.24
Sulphur	2.23	16.0	7.17
Nitrogen	0.9713	14.0	14.41
Phosphorus	4.50	31.0	6.89
Mercury	7.03	99.9	14.21
Cadmium	3.94	55.9	14.19

In the case of seven of these elements the relation between densities and the atomic weights is practically the same, averaging 14.4. For the remaining elements it is also virtually the same but much smaller than in the preceding case, the number 7.1 being about one-half the former number.

Another, and more usual, mode of stating this relation is that the atomic weights are proportional to the densities. Thus:

$$M : M' : : d : d'$$

where d and d' are the densities and M, M′ represent the atomic weights, or in the further extension of the law the molecular weights.

Theory of Avogadro.

Gathering together the facts which we have been discussing, we find that the volumes of all gases vary alike with changes of pressure and that the same is true for changes of temperature. Again the relation between the combining volumes of gases is a simple one and the specific gravities of the elementary gases are proportional to their atomic weights. There would seem to be but one explanation of these facts, one cause underlying them all, if the atomic theory is true. Dalton saw the necessary deduction and stated it but challenged the truth of the facts. These equal volumes of gases must contain the same number of ultimate particles. This was re-stated a year later, in 1811, by Amadeo Avogadro and it is generally known as Avogadro's Theory though Debus would call it, and with some justice, the Dalton-Avogadro theory. Three years later, in 1814, Ampere also announced the same conclusion as having been reached by him, being in ignorance of the writers who had preceded him. In fact, so simple is the deduction that it would seem strange if many had not clearly drawn it. And yet the support it gave to the atomic theory and its great importance were not duly recognized. The ultimate particles of the theory were not of necessity atoms but might be any minute portions, divisible or indivisible. Some accepted the law of volumes and sought to substitute it for the atomic theory. Berzelius, and others under his lead, caught the idea at first and made use of it, but misinterpreting, or rather misstating the theory, speedily encountered difficulties and contradictions and the theory was relegated to a subordinate place with them. Dalton rejected the idea because of exceptions and inconsistencies which he could not explain and thereby lost his claim to part in the theory. It was not until 1858 that Cannizzaro insisted upon the immense importance of this theory and made use of it to rescue the physical constants of chemistry from a state of unhappy confusion.

Distinction between Atoms and Molecules.

A prime obstacle in the way of the acceptance of the theory of Avogadro lay in the lack of a clear distinction between the varieties of ultimate particles. It was known that these were of two kinds, particles of elements and particles of compounds, but they were not distinguished from one another, and speaking of and treating them alike necessarily bred confusion of ideas. The word atom was used interchangeably for both kinds of particles and hence did not mean always the simple indivisible ultimate particle. With that idea fixed, the other particles made up of atoms, whether in an elementary gas or in a compound, would have been clearly differentiated.

Avogadro had made a clear distinction and suggested two names. When a substance splits up in its conversion into the gaseous state it is divided into a number of smallest particles which he called *molecules integrantes* or *constituantes*. These he defined as particles of matter which were so far apart that there was no longer any mutual attraction exerted and they were merely subject to the repelling action of heat. These particles he regarded as groups of several individual atoms (*molecules elementaires*) united by mutual attraction. This is, of course, in part the present distinction which is drawn between molecules and atoms and is indispensable in all chemical theories. It would have been of immense service if the suggestion of Avogadro had been followed, but it seems to have received scant notice. It is difficult to account for the blindness of such leaders as Berzelius and Dalton and Davy, except on the ground that it was at a formative period of the science and the general conditions chaotic.

Application of the Distinction.

The distinction was absolutely essential for the truth of Avogadro's theory. If his ultimate particles were atoms, then the theory failed to hold good in a number of cases. If they were compound, or molecules, then the explanation served. Thus experiment shows that 1 volume of oxygen and 2 volumes of hydrogen unite to form 2 volumes of water. But if each volume had an equal number of atoms and 1 oxygen atom was in each particle of water, it would manifestly be impossible that there should be formed more than 1 volume of water. Again, 1 volume of hydrogen and 1 volume of chlorine produced 2 volumes of hydrochloric acid, but the same reasoning would show that there could not be more than 1 volume of hydrochloric acid. It was from such reasoning as this that Dalton rejected the hypothesis of the existence of equal numbers of particles in each volume. If now, it is assumed that each particle of oxygen, of hydrogen and of chlorine was not an atom but a molecule containing 2 atoms, then the theory that the volumes contained equal numbers of particles becomes entirely probable and accords with the belief in combination by atoms as well as accounts for the relation between the specific gravities and the atomic weights. Avogadro's statement of the case was not worded as that above. He said that a molecule of water is made up of a half-molecule of oxygen and 2 half-molecules, or 1 whole molecule, of hydrogen. He did not expressly state what relations the particles, which he calls molecules, bear to the atomic weights, but he made it clear that he considered the combining weights only fractions, as a rule, of the molecules. It is evident that his mode of expression was not clearly understood, as Berzelius[1] in 1826 declared the views of Avogadro absurd since he sought to divide the atoms which were indivisible.

As to these particles, Davy[2] had espoused the view that the atoms first combine to form regularly arranged groups and then these unite, like elementary particles, to form various bodies. Ampere in 1814[3] advanced opinions similar to those of Avogadro. He also aimed at gaining some conceptions of the number and arrangement of the elementary atoms which form the molecules of different substances. The particles which he had in mind, however, were those which go to form crystalline bodies. Häuy used for these the name *molecules integrantes*. Avogadro, however, did not look with favor upon this extension of his theory. Avogadro's own efforts at extending his theory to cases where no observation of the density in the state of a gas had been made, or could be made, were

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[1] Jahresbericht, 1826, p. 80.

[2] Davy: "Elements of Chemical Philosophy," 1812.

[3] *Annal. de Chimie*, 90, 43.

also unfortunate and tended to bring discredit upon the theory.

Confirmation of the Theory.

Gradually confirmation of the truth of the theory of Avogadro came from various sides. Schroeder[1] based a certain argument in its support upon the physical properties of bodies, in particular the boiling-points of chemical compounds. Clausius[2] recognized the necessity for the theory from physical reasons arising from the mechanical theory of heat. Its acceptation by chemists, as Lothar Meyer says,[3] was because the molecular weights determined by its aid appeared the only numbers capable of serving as the basis of a theoretical speculation on all the different chemical transformations, and especially because this hypothesis established an analogy between the so-called elements and their compounds by regarding the former as compounds of similar atoms and the latter as compounds of dissimilar atoms.

Nascent State.

Several facts can be adduced to support the assumption that the ultimate particles of elementary gases are composed of atoms and are not single atoms. An argument can be drawn from the chemical fact that some of these gases behave very differently when they are just being liberated from compounds and when they are in the ordinary gaseous condition. In the first case they are said to be in the nascent state and they show far greater chemical activity. Thus hydrogen in its usual condition shows little tendency to combine with most other elements and compounds. On the contrary, if it is just being liberated from some preexisting compound it is capable of uniting immediately with a number of bodies and of bringing about very

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[1] "Die Siedhtze d. Chem. Verb." (1844), 27, 67, 138.

[2] *Pogg. Annalen*, **100**, 369 (1857); **103**, 645 (1858).

[3] "Modern Theories of Chem." (Eng. trans.), 1888, p. 12.

material changes in bodies with which it comes in contact. Similar facts have been observed with regard to oxygen, nitrogen and other elements. The only plausible explanation which has been advanced to explain these facts is that in the ordinary condition of these gases one is dealing with molecules consisting of at least two atoms, thus: HH, OO, NN, etc. As these atoms are already united with one another there is little or no tendency to effect a material change on any other body until they have been separated and so are free from the formation of fresh compounds. If the element is just being liberated from some compound, as when nitric acid acts upon zinc,

$$Zn + 2HNO_3 = Zn(NO_3)_2 + H_2,$$

then it may be assumed that each atom of hydrogen when set free from the molecule of nitric acid remains uncombined for a brief fraction of time and in this condition shows a greatly increased tendency to form compounds. If it meets with some other element, or group of elements, with which it can combine, immediate combination takes place. If no such body is present, then it combines with another hydrogen atom and thus forms a molecule made up of similar atoms. It must be borne in mind that there are no proofs of this. It is merely an hypothesis to explain the fact of greater chemical activity being exibited in one case than in the other. An argument then which involves so much assumption should not have too much reliance placed upon it. Some chemists contend that the hypothesis of a nascent state should be discarded altogether as needless, but so far, nothing more satisfactory has been suggested to explain the facts.

Ozone. To show that the simple hypothesis is not always satisfactory or accepted, it may be mentioned that there is a very active form of oxygen, called ozone, which is formed in many reactions when oxygen is liberated from certain compounds, as for instance from carbon dioxide, or when this element is acted upon by electricity, and in a number of other ways. This active form of oxygen, however, is not called nascent oxygen nor is it supposed to consist of single separate atoms. The fact that it exists free for appreciable lengths of time, of course, differentiates it from the ordinary nascent elements. Considerations of density have led chemists to conclude that in this case the molecule consists of three atoms. They then attribute the great energy exhibited by it to its instability and the ease with which it breaks up into two-atomed, or the ordinary oxygen, and a single-atomed, or nascent oxygen, which is supposed to be the energetic portion. There is much in the behavior of the body to lend strength to these suppositions.

This instance is cited here merely to show the amount of assumption involved and the doubt which can be thrown upon all arguments from a presumed nascent state. It will be observed that in an argument intended to strengthen the Avogadro theory, this theory itself is appealed to in order to establish the presence of 3 atoms in the molecule of ozone, ordinary oxygen being assumed to have 2 atoms to the molecule, and in the decomposition of ozone the single atom set free is said to exercise the powerful oxidizing action,—all of which is plausible and may be true, but certainly is without direct proof. Since there is entire ignorance as to the density of active hydrogen or active nitrogen it is manifestly a possible assumption that these also are molecules of two or more atoms. At bottom the facts are that various gaseous elements exist in two or more forms which differ in physical properties and in chemical activity. This existence of an element in two or more different forms is known as allotropism and may be observed in the liquid and solid as well as the gaseous states. The only plausible explanation of this phenomenon which has been offered involves the atomic hypothesis and assumes that the ultimate particles of these elements are in the different cases made up of different numbers of atoms.

Intermolecular Work.

Returning now to the hypothesis that the particles in elementary gases are really molecules made up of at least two atoms there are certain physical facts which may be adduced to confirm this belief. In bringing forward these arguments the kinetic theory of gases is supposed to be true. The total energy of the molecules of a gas represents the amount of heat absorbed by the gas. When the molecule is looked upon as a material point this energy can only be progressive motion. Taking this, it is not difficult to calculate the relation between the specific heat of a gas at constant volume and that at constant pressure. Let h and h' represent these two specific heats respectively, then this ratio is $\frac{h'}{h} = c$. According to theory for a material point without moving parts, $c = 1.67$. In the case of most gases examined the observed value is less than this theoretical one, c being equal to 1.405. Thus it is seen that when the volume remains unchanged more heat is actually required to raise the temperature of a gas than the theory demands. A portion of the heat therefore disappears and it may be that this is transformed into motion between the atoms which compose the molecule, or what is called intramolecular work. If there is but one atom and so no intramolecular motion possible, then the ratio observed should be the same as the theoretical, namely 1.67. This ratio has been observed in the case of a few gases only, as gaseous mercury, cadmium and possibly other metals, also argon, helium, etc. These may be assumed to have molecules of one atom. In the others there would seem to be a greater number of atoms.

Again Kundt and Warburg[1] have made use of the propagation of sound in gases. Here also evidence can be gotten as to internal motion in the particles and the evidence accords with that secured by the method just mentioned. Thus mercury vapor in sound experiments also acts as if the particles were material points.

Practical Use of the Theory.

Enough then is known to make it very probable that gases consist of compound particles and rarely of indivisible atoms. In using Avogadro's theory in the determination of atomic weights it becomes necessary to assume one molecular weight as known. Since the molecular weights are proportional to the densities we have

$$m : m' :: d : d'$$

where m and m' are the molecular weights and d and d' are the densities. Then,

$$m' = d' \times \frac{m}{d}.$$

To solve this, d and d' are densities which can be determined by experiment but m cannot be so determined. Still if one such molecular weight be assumed then all others can be based upon it. Hydrochloric acid is the gas whose molecular weight is assumed as a standard. This compound contains by weight 35.4 parts of chlorine to 1 part of hydrogen. A smaller figure would necessitate representing the atomic weight of hydrogen as less than unity, which is of course not an impossibility if that which has

[1] *Ber. d. chem. Ges.*, 1875, p. 945.

hitherto been assumed as the atomic weight of hydrogen be in reality the weight of more than one atom. On the other hand it may be said that no facts are known that require the selection of a number greater than 36.4 (1 + 35.4) for the molecular weight of hydrochloric acid. Should facts become known which require a smaller figure, then all of the determinations of molecular weights must be changed in proportion. With this assumption the above equation becomes

$$m' = d' \times \frac{36.4}{1.247} = d' \times 28.57.$$

This figure, 28.57, should be the quotient obtained by dividing the molecular weight of any known gas by its specific gravity. Experimental errors, however, cause a slight variation from this. The number, 28.88, is more nearly the average of many results.

Results as to Gaseous Molecules.

By means of this method the molecules of most elementary gases have been found to consist of two atoms. This may be deduced from the fact that in every case of combination of elementary gases, where one volume of one gas is taken the resulting compound occupies two volumes. Certain elements as mercury, argon, helium, etc., in the form of vapor have apparently only one atom in the molecule, as has already been mentioned. Others as sulphur, phosphorus, arsenic, etc., have molecules containing different numbers of atoms according to the temperature to which they are heated. Thus sulphur at 860° has a density of 2.23 which corresponds to two atoms in the molecule, at 524° its density is three times as great, which would lead to the conclusion that the molecule contains six atoms. Another instructive example is seen in the case of iodine. The specific gravity of iodine vapor at low temperatures is 8.8 which corresponds to a molecular weight of 254, or a molecule of two atoms. At 1027° this density becomes 5.8, at 1468° it is further reduced to 5.1. At the highest temperature at which the observations could be carried out it was found to be 4.5 which is very nearly half the first specific gravity and indicates a molecule of one atom. It has not been possible to go beyond this point. This has been taken as a possible indication that at very high temperatures all gases consist of molecules made up of single atoms.

Supposed Exceptions to the Theory.

A similar decomposition of the molecules of compound bodies when vaporized at high temperatures has been shown in several interesting cases by vapor-density determinations, and the dissociation sometimes confirmed by additional experimental observations. These were at first supposed to be exceptions to the working of the Avogadro theory. Ammonium chloride can be formed by the combination of one volume of ammonia and one volume of hydrochloric acid. The analysis of this compound gives the proportion between the elements as nitrogen 14, hydrogen 4, and chlorine 35.4, or by atoms as nitrogen 1, hydrogen 4, and chlorine 1. The density of a molecule of this compound, that is, of as much as would occupy the same space as a molecule of hydrogen, would be 53.4. But the density as determined by experiment is only 26.69, or half as much as would be expected. This would mean, if the theory is correct, that in ammonium chloride the atoms of nitrogen and chlorine are only half so large as in all other known compounds and the formula would be $N_{1/2}H_2Cl_{1/2}$, or the formulas of the other compounds of nitrogen and chlorine would have to be doubled, nitrogen being taken as 7 and chlorine as 17.7

and the formula for ammonium chloride being taken as NH_2Cl. Then the densities of these other compounds would show them all to vary from that required by the theory. Unless some other explanation is found the dilemma is a serious one, either ammonium chloride is an exception or the other compounds are, and exceptions are fatal to theories. Some time passed before a satisfactory explanation was found but it can now be shown that when ammonium chloride is volatilized the vapor is not that of the ammonium chloride but of the mixed gases ammonia and hydrochloric acid. Hence the density will be the mean of these two $\left(\frac{17-36.4}{2}=26.7\right)$ and not that of the two combined (53.4) and this accords with the observed density.

Phosphorus pentachloride, PCl_5, was also once regarded as an exception but a similar splitting up of the molecule into PCl_3 and Cl_2 can be proved. In this case the dissociation is a gradual one with the rise of temperature and hence varying densities are observed. Recent experiments seem to show that this and the above dissociation are due to the presence of traces of water, and that they do not take place in the perfectly dry gas at moderately high temperatures.[1] The important fact to be noted just here is that the method of densities combined with Avogadro's theory reveals this dissociation and its extent. Several other cases are known in which the observed density varies from the theoretical but they are capable of being explained in the same way as the instances cited and indeed in nearly all of these there is convincing proof that such explanation is the correct one. These apparent exceptions then are

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[1] *J. Chem. Soc.* (London), 1900, p. 646.

really strong confirmations of the truth of the theory. While this is apparent now it must be borne in mind that for many years no explanation of these exceptions was known and they tended greatly to discredit the theory. These points will, however, be taken up later.

Law of Specific Heats.

In the year 1819 Dulong and Petit published[1] the specific heats of 13 chemical elements adding the observation that these specific heats were as a rule inversely proportional to the atomic weights. The consequent deduction from this is that the specific heat is directly proportional to the number of atoms contained in the unit weight. This then gives a method of determining the number of atoms in molecules of solids. The table given by Dulong and Petit was as follows:

Element.	Specific heat.	Relative weights of atoms.	Weight × specific heat.
Bismuth	0.0288	13.30	0.3830
Lead	0.0293	12.95	0.3794
Gold	0.0298	12.43	0.3704
Platinum	0.0314	11.16	0.3740
Tin	0.0514	7.35	0.3879
Silver	0.0557	6.75	0.3759
Zinc	0.0927	4.03	0.3736
Tellurium	0.0912	4.03	0.3675
Nickel	0.1035	3.69	0.3819
Iron	0.1100	3.392	0.3731
Cobalt	0.1498	2.46	0.3685
Sulphur	0.1880	2.011	0.3780

As to this table it must be stated first that there were several errors which were afterwards corrected by Regnault. In the case of tellurium and cobalt the specific heats were too low. The atomic weights were given with oxygen as unity. To compare these with those of Berzelius they must be multiplied by 100. On making

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[1] *Ann. chim. phys.*, **10**, 395–413.

the comparison it will be seen that a number of them, as those of zinc, iron, nickel, copper, lead, tin, gold, and tellurium were only half as large as those given by Berzelius. In choosing this smaller number Dulong and Petit were influenced by the notable regularity observed in connection with other atomic weights. In determining upon an atomic weight by combining proportions there were often two or three numbers to choose between, which, however, bore a very simple relation to one another. Hence the choice was always to some extent arbitrary. The regularity observed by Dulong and Petit, and called by them a law, might most justly be used to arrive at a decision between such combining proportions, obtained by analysis. These authors remark that " the mere inspection of the numbers obtained points to a relation so remarkable in its simplicity as to be at once recognized as a physical law, susceptible of being generalized and extended to all elementary substances. In fact the products in question which express the capacities for heat of atoms of different natures are so nearly the same for all that we cannot but attribute these very slight differences to inevitable errors, either in the determination of capacities for heat or in the chemical analysis." The law was further stated by Dulong and Petit as follows: " The atoms of all simple bodies have precisely the same capacity for heat." While the former mode of statement bore especially upon the determination of atomic weights, which was the burning question of the time, and so, was the point of view from which the law was most commonly regarded, the latter is most significant as regards the atoms and their nature and hence is most important from the standpoint of this present study.

Difficulties in the Way of Acceptance. As a simple generalization based upon easily substantiated facts it might have been expected that the law of Dulong and Petit would have been immediately and widely accepted by chemists but such was not the case. One cause for this lay in the errors and inaccuracies mentioned above, and further in the apparent exceptions which soon came under observation. Another cause is to be found in the influence of Berzelius, the weight of which was thrown against its immediate acceptance. He recognized the great importance of the law for theoretical chemistry but thought that some of the atomic weights assumed by the authors would give improbable relations for the compounds of these elements. Thus, for instance, the atomic weights of zinc, iron, nickel, copper, lead, tin, gold, and tellurium would make the oxides of those metals monoxides, ZnO, FeO, etc., while Berzelius regarded them as dioxides. It was possible, of course, that the relations hitherto accepted for these elements, reasoned from analogy, did not exist. It was possible that the generalization of Dulong and Petit did not hold in some cases and to decide this the investigation should be extended. As he could not arrive at a decision as to this he determined for the time to retain his former atomic weights.[1]

Application to Compounds. Berzelius had expressed the desire for the application of the generalization of Dulong and Petit to compound bodies. This was first done by F. Neumann[2] in the year 1831, who showed that equivalent quantities of compounds having analogous composition have the same specific

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[1] Berzelius: "Jahresbericht," I, 19, and XXI, 6.

[2] Pogg. *Annalen*, **23**, 1.

heats. This was not due to the bodies having the same crystalline form. It was true even when the crystalline form differed. Neumann's extension of the law may be stated in the same form as the law, namely for compounds of analogous composition the specific heats are inversely proportional to the molecular weights of the compounds, or the molecules of different compounds have equal capacity for heat. The product of the molecular weight multiplied by the specific heat is then a constant quantity. Thus:

Lead chloride, $0.0664 \times 459.48 = 19.62$;
Lead bromide, $0.0533 \times 365.92 = 19.50$;
Lead iodide, $0.0427 \times 459.48 = 18.40$;

or again,

Calcium chloride, $0.1642 \times 110.06 = 18.07$;
Strontium chloride, $0.1199 \times 158.04 = 18.95$;
Barium chloride, $0.0902 \times 207.64 = 18.73$.

From a large number of similar results the deduction can be made that an element, whether in the free state or in combination, possesses the same specific heat. Thus, take the case of lead iodide. If the specific heat of lead is multiplied by its atomic weight we have

$$0.0307 \times 206.4 = 6.34,$$

and so for iodine,

$$0.0541 \times 126.54 = 6.85.$$

There are, however, 2 atoms of iodine in lead iodide, hence

$$6.85 \times 2 = 13.70.$$

The specific heats of the constituents of lead iodide are therefore

$$6.34 + 13.79 = 20.04.$$

The specific heat of lead iodide determined by experiment is 19.62 which agrees well with the other and so the above deduction is justifiable. From this it is easy to see how the specific heat may be used to determine the number of atoms in a molecule and so to make it possible to choose correctly between two or more possible weights for the atom obtained by analysis. The determination of the specific heat involves so many difficulties that the direct determination of the atomic weight by means of it is only an approximation.

Experimental Difficulties.

As has been stated, the first work of Dulong and Petit was far from accurate, and the results were quite properly received with caution and conservatism by Berzelius and others. There were many experimental difficulties in the way of the determinations. A high degree of purity in the substance tested was essential, and furthermore as the methods became more accurate it was seen that the specific heat of a substance was not constant for all changes of conditions. Hence, in 1834,[1] Avogadro spoke of the law as an approximation only. The very careful work of Regnault, beginning in 1840, showed in how far this was true. It is known now that the specific heat increases with increase of temperature; that for the same substance it is greater in the state of a liquid than in the solid state. In the case of metals, it is diminished by rendering them more dense, as by pressure, and, in the case of the allotropic forms of an element, the specific heat is often different even under similar conditions. These matters demanded an explanation before the generalization of Dulong and Petit and of Neumann could be accepted, and a beneficial influence be exerted upon chemical theory. The painstaking investigations of Regnault, embracing a large number of substances, confirmed the generalization of Neumann as to a large number of compounds, and proved that the law applied in the case of most of the elements

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[1] *Ann. chim. phys.*, **55**, 80 (1834).

examined—about forty in all. The following table will illustrate this:

Element.	Specific heat.	Atomic weight.	Sp. ht. × at. wt.
Lithium	0.941	7	6.6
Sodium	0.293	23	6.7
Magnesium	0.250	24	6.0
Potassium	0.166	39	6.5
Iron	0.114	56	6.4
Copper	0.0952	63.1	6.0
Zinc	0.0955	65	6.2
Silver	0.0570	108	6.2
Tin	0.0562	117.4	6.6
Gold	0.0324	197	6.4
Mercury	0.0317	200	6.3
Lead	0.0307	207	6.4
Bismuth	0.0308	207.3	6.5

From many determinations it is seen that the number obtained by multiplying the specific heat by the atomic weight ranges from 5 to 7, averaging about 6.25. This then represents the capacity of the atom for heat and is called the atomic heat. The variations in this number, which according to law should be a constant, may be assigned to various causes. In the first place, the atomic weights are far from being accurately known, and are subject always to errors of observation, as are also the determinations of the specific heats. Again, some of the elements have never been obtained in a condition which could be with certainty regarded as pure. Furthermore, as Regnault observed,[1] the determination is uncertain, as it includes several unknown factors which so far can not be discriminated between, as the latent heat of expansion and of fusion, which is gradually absorbed by bodies as they frequently soften long before the temperature is reached which is regarded as their melting-point. Thus some of the heat goes to preparing the way for a change of aggregation by diminishing the force of cohesion. It is the effect of the sum of all these changes, and perhaps

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[1] *Ann. chim. phys.*, 3 ser., **26**, 262.

of others as yet unrecognized, which is called the specific heat, and yet, as Wurtz says, it is surely remarkable that in spite of the complexity of the phenomena so simple and so great a law should be evolved from such determinations.[1]

Apparent Exceptions. It will render this part of the subject somewhat clearer if the cases be examined in which wide variations from the average atomic heat have been observed. The elements exhibiting these variations are chiefly carbon, silicon and boron.

	Specific heat.	Temperature.	Atomic weight.	Atomic heat.
Carbon :				
a. Diamond	0.064	at —50.5°	12	0.77
	0.096	at —10.6°	12	1.15
	0.113	at —10.7°	12	1.36
	0.132	at —33.4°	12	1.58
	0.153	at —58.4°	12	1.84
	0.177	at —85.5°	12	2.12
	0.222	at 140.0°	12	2.66
	0.273	at 206.1°	12	3.28
	0.303	at 247.0°	12	3.64
	0.441	at 606.7°	12	5.29
	0.449	at 806.5°	12	5.39
	0.459	at 985.0°	12	5.51
b. Graphite	0.114	at 50.3°	12	1.37
	0.199	at 61.3°	12	2.39
	0.297	at 201.6°	12	3.56
	0.445	at 641.9°	12	5.34
	0.467	at 977.9°	12	5.60
c. Charcoal	0.194	0 to 99.2°	12	2.33
	0.239	0 to 223.6°	12	2.87
Silicon :				
Crystallized	0.136	at —39.8°	28	3.81
	0.170	at 21.6°	28	4.76
	0.183	at 57.1°	28	5.12
	0.190	at 86.0°	28	5.32
	0.196	at 128.7°	28	5.49
	0.201	at 184.3°	28	5.63
	0.203	at 232.4°	28	5.68
Boron :				
Crystallized	0.192	at —39.6°	11	2.11
	0.238	at 26.6°	11	2.62
	0.274	at 76.7°	11	3.01
	0.307	at 125.8°	11	3.38
	0.338	at 177.2°	11	3.72
	0.366	at 233.2°	11	4.03

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[1] "Atomic Theory," p. 126.

Manifestly, at ordinary temperatures, these elements do not even approximately follow the law. The specific heats, however, increase with the temperature, and at high temperatures they are in accord with what would be required by the law. They do not increase beyond this point. The specific heats vary with the temperature, therefore, and for each element there seems to be a temperature beyond which variations are slight and at which the specific heat is approximately in accord with the law. Hence the generalization can be assumed to be a law only within certain fixed limits of temperature. From all of this it is seen that the law of Dulong and Petit is only an approximation, and can only be such until a distinction can be made between the heat that goes to increase the temperature, and that which is utilized in internal work in the molecules. In the case of solids and liquids the external work is probably very small. On the other hand, the internal work will vary with the size of the molecule and may amount to a good deal. The fact that it does not cause a greater divergence from the law on the part of many elements would seem to indicate that it also, like the specific heats, is inversely proportional to the atomic weights.

In making use of the law of Dulong and Petit for deducing atomic weights, it is necessary to prove that the specific heat has been determined at temperatures between which it shows but slight variations, and the range of temperature should be a wide one.

Failures of the Law.

In conclusion, certain further variations may be mentioned. The law does not hold good for gaseous elements, like hydrogen and oxygen, nor for gaseous compounds. In the case of several elements, the specific heats in the solid state are about twice as great as in the gaseous state.

These facts but emphasize the statement already made that the so-called law of Dulong and Petit is in the truest sense only an approximation, and so long as the determinations yield results which are the sum of several unknown quantities, it is unscientific and untrue to call the generalization a law. It is far from proved that the atoms of the various elements have the same capacity for heat. It can only be maintained that under certain fixed conditions, and judged by our systems of measurement, the variations from a certain constant are not great, and consequently this constant may be used in deciding the number of atoms in a molecule and in coming to a decision between two or more possible atomic weights.

Hypothesis of Kopp.

It is of importance here to note the hypothesis suggested by Kopp. It was offered in explanation of the wide deviations shown by certain elements as carbon, silicon and boron before the influence of temperature upon them was known, and so to make it consistent with later knowledge. Lothar Meyer[1] has modified it somewhat. Let it be supposed that elementary atoms are composed of still smaller parts, which may be called particles, and that at low temperatures the motion of these particles is that of a single system. At higher temperatures this system is resolved into others containing a smaller number of particles. And finally, at still higher temperatures this resolution takes place to such an extent that each particle moves freely and independently. Therefore at temperatures at which the atoms do not obey the law of Dulong and Petit the particles do not move singly but in groups of several such particles, each of which requires the same amount of heat to raise its temperature through

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[1] "Modern Theories," p. 93.

1° as is required by the single particle of an atom subservient to this law. For example, an atom of carbon in the form of diamond, possessing at —50° C. an atomic heat of 0.76, contains half the number of groups of particles which it contains at 27.7°, at which temperature its atomic heat is twice as large, *viz.*, 1.52. The different groups are not of necessity twice as large but must, on an average, contain twice as many particles at —50° C. as they contain at 27.7° C.

Tilden[1] has made certain specific heat determinations for nickel and cobalt at very low temperatures (—78.4° and —182.4°) which led him to think that at absolute zero the products of the specific heats multiplied by the atomic weights would be identical or differ only by the very small amounts due to experimental error. Further experiments with silver, copper, iron and aluminum failed, however, to justify this expectation.

Law of Isomorphism.

Another generalization announced in 1819, used for the determination of the number of atoms in solid molecules, was that called the Law of Isomorphism and discovered by Mitscherlich. This also has proved to be no law in the truest sense, but an approximation and one of far more limited application than that of Dulong and Petit. Yet at first it was hailed with acclaim and was considered one of the most important aids toward determining the number of atoms in the molecule.

The work of Mitscherlich had for its basis many observations of a long line of chemists, going back even to the time of Stahl, for chemists having few reliable criteria at command had long observed the crystal forms, especially of minerals, most closely as affording an indi-

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[1] Bakerian Lecture before Royal Society, March 8, 1900; *Chem. News*, 81–133.

cation of similarity or unlikeness of composition. Bodies which crystallized in different forms even though otherwise alike were often believed to differ in composition. And yet against this conclusion were known such facts as the qualitative and quantitative identity of arragonite and calcite which differ in crystal form; and of anatase and rutile. Hauy had maintained that the crystalline figure was dependent upon the form of the smallest particle and that these must have a constant composition. This was disputed by Berthollet and led to a prolonged discussion.

Early Theories.

Several theories were advanced by earlier chemists to explain the fact that two or more bodies may have the same crystal form though differing in composition. Probably the most noteworthy one at the time that Mitscherlich announced his theory was that the form was assumed through the influence of some impurity. Thus the natural occurring carbonates of magnesium, zinc, iron, etc., crystallize in the same form as calc-spar and it was believed that this was due to the presence of small amounts of calcium carbonate in these bodies, but when calcium carbonate itself crystallized as arragonite this was supposed to be due to its containing some strontium carbonate, this having a superior determining force to calcium carbonate.

When it was shown that strontium carbonate was not to be detected in many specimens of arragonite, Gay-Lussac drew attention to the growth of one substance upon a crystal of another as a particularly important phenomenon in considering this question. Thus a crystal of potassium alum placed in a solution of ammonium alum would continue to grow without change of form. This he said must be due to the fact that the two alums have particles of the same form and are endowed with the same energies. In 1817 Beudant returned to the theory of the form of the crystal being determined by some mixture or impurity, basing his views especially on the behavior of the salts then called vitriols. Thus, in a mixture of copper and iron sulphates, the crystals take the form of the latter, even though it may form but 9 per cent. of the mixture. In mixtures of zinc and iron sulphates, the latter determines the form when present to the amount of 15 per cent. In mixtures of the three, as little as 3 per cent. of iron sulphate is sufficient to determine the form. In these experiments no account was taken of the water of crystallization.

Theory of Mitscherlich.

These theories were substituted in 1819 by the theory of Mitscherlich.[1] He had been busied with an investigation of the phosphates and arsenates. At the beginning of his report upon this work to the Berlin Academy, he wrote that it seemed to him certain that the agreement in chemical behavior which the compounds show that are constituted in equal proportions and with like crystal form may scarcely be referred to the agreement in crystallization as its ground; that they lead us rather to a more deeply hidden cause by which both the composition of the body and the agreeing crystallization are to be explained. In the case of phosphate and arsenate of the same base he found the crystal form to be identical. This he at first attributed to their containing the same number of atoms. He investigated the sulphates and found that where they crystallized differently they had different amounts of water of crystallization. When they crystallized together or in mixtures they always contained the

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[1] Abhandlungen d. Berl. Akad., 1819, p. 426; *Ann. chim. phys.*, 14, 172.

same amount and so assumed the form of the sulphate which corresponded to this. Further study convinced Mitscherlich that the number of the atoms was not the only thing to be considered but that their nature was a controlling factor. He recognized that there were certain elements, called by him isomorphous, which gave compounds of identical crystal form by uniting with the same number of atoms of other elements. These he placed in groups. This is to be noticed as one of the earliest recognitions of families of elements. This identity of crystal form was dependent upon a similarity in the arrangement of the atoms. If the conditions of crystallization were changed, different forms might be obtained. This would account for the dissimilarity of form in the case of arragonite and calc-spar. This he styled polymorphism. In 1821 he formulated his hypothesis as follows:[1]

An equal number of atoms combined in the same manner, gives the same crystalline form; this crystalline form is independent of the chemical nature of the atoms, depending only on their number and arrangement.

Of course the chemical nature of the elements determines the number and arrangement of the atoms in the molecule and so influences the crystalline form, but Mitscherlich believed it to be without direct influence.

It is clear that if this hypothesis is true it affords a most valuable method for determining the number of atoms in the molecule and so of deciding upon an atomic weight which may be in doubt. Given a compound containing a known number of atoms with known atomic weights, and the number of atoms in any compound crystallizing in the same form could be determined. Berzelius made use of the law of isomorphism in deciding the atomic

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[1] *Ann. chim. phys.*, 19, 419.

weights for his tables and placed more confidence in his results obtained by this method than by any others. But he found that in this also there was much uncertainty and was forced to alter in a number of cases the figures selected as the atomic weights.

Conclusions Drawn Uncertain.

There were several reasons for this uncertainty in conclusions drawn from the law of isomorphism. Many instances may be adduced in which the compounds showing identity of crystal form undoubtedly contain different numbers of atoms. Again similarity in number and arrangement of atoms does not always produce identity of form. In the effort at eliminating such cases, which do not follow the generalization, the definition of isomorphism has been changed and limited. Thus it was stated that mere identity of form was insufficient to prove isomorphism. It should further be required that the substances should crystallize together and in varying proportions be able to build up one and the same crystal; that is, that a crystal of one substance should continue to grow in a solution of the other. This possibility of overgrowth has been accepted by many as the best proof of isomorphism but this involves immediately an anomaly since this overgrowth is especially noted in compounds of potassium and ammonium where equality of atomic composition is impossible.

Complexity of the Problem.

There are many facts which render the correlation of crystal form and chemical composition a very complex problem. There has been some attempt at differentiating between the facts and classifying the data. Thus there are what have been called the phenomena of "homeomorphism" where there is a difference in composition but an approximation as to form. Many instances of homeomorphism might be given; thus arragonite, $CaCO_3$, and nitre, KNO_3; baryte, $BaSO_4$, potassium permanganate, $KMnO_4$, and potassium perchlorate, $KClO_4$. Again, as Dana has pointed out, there are instances with still greater dissimilarity of composition; thus, cinnabar, HgS, and susannite, $PbSO_4,3PbCO_3$; potassium hydrogen sulphate, $KHSO_4$, and feldspar, $KAlSi_3O_8$; etc.

It is manifest that mere nearness of crystalline form will not answer. It is probable that the limitation to the capacity for overgrowth does not bring any nearer the solution of the question as to the influence of atomic composition upon form. It would seem that a solution is to be reached only by most accurate determinations of angles of crystals, and the changes produced in these by varying the atomic composition. Work along this line has been done, and it is already evident that with a definite change of composition certain angles remain constant though others may be altered greatly. Further work along this line is very necessary and would seem to promise important results. The hypothesis of Mitscherlich is clearly not to be called a law, but is a generalization of somewhat uncertain and limited application, and while it has been a valuable aid in the determination of atomic weights, chiefly, as Wurtz[1] says, when its indications can be connected with positive intelligence drawn from the law of volumes or the law of specific heats, greater interest now attaches to the wider question as to the correlation in general between crystal form and atomic composition.

Electrochemical Equivalents.

Electricity had been used since the last part of the 18th century as a powerful agent for bringing about the decomposition of chemical substances. Thus the de-

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[1] Wurtz: "Atomic Theory," p. 148.

composition of water was studied by a number of observers, and a little later there followed the brilliant decomposition of the alkalies by Davy with the production of the alkali metals. In 1803 Berzelius and Hisinger showed that the passage of a current of electricity through a salt separated the acid from the base, the former being found at the positive pole and the latter at the negative. Davy's work confirmed this, but this work was almost exclusively qualitative until Faraday studied the changes quantitatively and detected the connection which existed with the combining numbers of the elements, thus deducing his law of electrical equivalents.

In 1834 Faraday[1] showed that the electrochemical decomposition is a fixed quantity for a definite amount of electricity. Out of various compounds subjected to this decomposition, as water-dissolved hydracids, fused metallic chlorides, etc., equal amounts of the same element were separated by the expenditure of the same amount of electricity. The amounts of different elements thus separated correspond with their ordinary chemical equivalents or combining numbers. Hence he called these numbers the electrochemical equivalents. They may be further regarded as the relative weights of the atoms. It is easy to see how this method of determination might be used in connection with the methods already mentioned to confirm their results. But after all, this is only another method of analysis and without a knowledge of the number of atoms in the molecule of the compound, the solution of that problem is as far off as ever. Faraday pointed out that the electrochemical equivalents obtained for bodies which were capable of direct electrolysis did not agree in many cases with those assumed by Berzelius nor with those ob-

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[1] *Phil. Trans.*, 1834, p. 77.

tained by the use of the specific heats, etc. For instance, the electrochemical equivalents of oxygen and chlorine did not stand in the same ratio as the weights of equal volumes of these two elements.

Freezing-Points of Solutions.

Several methods have been devised in more recent years for determining the number of atoms in molecules of solids dissolved in liquids. When a solid is dissolved in a liquid, the freezing-point of the solvent is lowered. The experiments of Raoult have shown that this bears a definite relation to the molecular weight of the dissolved substance. The law deduced by Raoult was that for every molecule of a compound dissolved in 100 molecules of a liquid, the freezing-point is lowered by an approximately constant amount, namely, 0.62°. If $P =$ weight of compound, $L =$ weight of solvent, $E =$ lowering of freezing-point, $m =$ molecular weight of compound, then

$$\frac{P \times M}{L \times 100M} E = 0.62^\circ, \text{ or } m = \frac{P \times 62M}{L \times E}.$$

This so-called law does not hold good for some classes of substances, as inorganic salts, strong bases and acids. It is chiefly used with organic substances and organic solvents. The two most commonly used solvents are benzol and acetic acid.

Vapor-Pressures and Boiling-Points.

It is easy to see that a similar generalization could probably be drawn as to the vapor-pressures and boiling-points of solutions. The solution of a substance lowers the vapor-pressure. This also was examined by Raoult and others and the following generalization deduced. The relative lowering of the vapor-pressure is proportional to the ratio of the number of molecules in solution.

In the case of the boiling-point, we find it raised and the elevation of the boiling-point is proportional to the concentration. Where we have equally concentrated solutions of different substances, the increase in the boiling-point is inversely proportional to the molecular weights of the substances. Lastly it has been shown by Pfeffer and van't Hoff that interesting relations obtain between the osmotic pressure and the molecular weights of dissolved substances.

Atomic Theory in Doubt.

The lack of uniformity in the atomic weights and the general uncertainty surrounding them, which prevailed during the third and fourth decades of the 19th century, weakened greatly the confidence placed in the atomic theory so that many were ready to abandon it, and, eschewing theory, devote themselves solely to the practical side of the science. By such, the name combining weight was preferred to that of atomic weight. The generalizations of Dulong and Petit and of Mitscherlich were beset with difficulties and their exceptions were unexplained. The theory of Avogadro failed to clear up matters so long as no distinction was made between atoms and molecules. Each method seemed to yield results at variance with the others. Regnault, using the specific heats, called his "equivalents thermiques"; Rose and Marignac gave tables of "isomorphic equivalents", and there were the "electro-chemical equivalents" of Faraday. The Berzelian table had oxygen equal to 100 for its standard; the Gmelin table had hydrogen equal to 1. It is not strange that confusion reigned.

Atom and Molecule.

In 1837 Dumas[1] drew attention to the distinction between atoms and molecules. Yet he thought the idea of atomic weight

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[1] "Philosophy of Chemistry," 1837.

an indeterminate one and that no confidence was to be placed in it. The equivalents or combining numbers could be determined by analysis. If it were possible he would forever banish the word atom from chemistry since he was persuaded that it went beyond that which could be fixed by experiment. Liebig[1] in 1839 expressed himself in a similar manner. The equivalents, he said, would never change but he very much doubted whether chemists would ever be agreed as to the numbers by which the relative atomic weights should be expressed. The study of chemistry would be made greatly easier when all chemists decided to return to the use of equivalents.

It is not clear just how the return to the equivalents, contended for years before by Wollaston, was to do away with the confusion and lack of uniformity. It is evident that there would have to be a choice made between possible equivalents just as it must be made between possible atomic weights and there were no better guides to a choice in the one case than in the other. The neglect of the practical distinction between atoms and molecules continued for two more decades. Thus there is no apparent distinction made by Graham and others of his time, but those who were especially busied with organic chemistry were beginning to see more clearly. The unitary system of Gerhardt was coming in, displacing the dualism of Berzelius.

The systems of numbers in use gradually narrowed down to two, though variations as to special elements were not infrequent. These two chief systems were those of Berzelius and of Gerhardt. One of the foundations of the Berzelian system was the law of volumes as erroneously interpreted by him. This erroneous interpretation was

[1] *Ann. d. Pharm.*, **31**, 36.

practically overthrown by the work of Dumas and Mitscherlich upon vapor-densities. Mitscherlich's discovery of isomorphism caused Berzelius to make important changes in his earlier tables. He introduced the term 'double atoms' to allow for the exceptions to his idea of the law of volumes and to make certain that his atomic weights correspond with the numbers more generally accepted by the leading chemists. Thus hydrogen, nitrogen, chlorine, bromine and iodine were classed among the double atoms and were supposed to enter into combination in pairs, each pair representing what other chemists styled an equivalent. This was very awkward and did not appeal to the better judgment of most chemists. Dalton and Thomson, Gay-Lussac, Wollaston and lastly Gmelin, whose "Handbook" exercised a wide-spread influence, adopted the numbers obtained from equivalent quantities which enter into combination. The law of volumes was entirely discredited. Chemical analysis was largely relied upon. The widespread popularity of Gmelin's "Handbook" secured a large following for his system of weights. In the earlier editions of the Handbook, these were called by the unfortunate name of mixing weights (Mischungsgewichte). The name was later changed to atomic weights without making any material change in the notation. The chief point of discussion between Gmelin and Berzelius lay in the correctness of the weights which were halved by Berzelius and the propriety of the assumption of double atoms, these double atoms being the true atoms in the opinion of Gmelin. The law of volumes was, he maintained, contradicted by experiment and therefore not a reliable guide in this matter. Again the half atoms never entered into combination and consequently their assumption was unnecessary. Berzelius would make the formula for water H_2O, hydrochloric acid H_2Cl_2, and ammonia H_6N_2. Gmelin would double the atomic weight of hydrogen and so simplify these formulas to HO, HCl, H_3N.

Gmelin ably defended his system in 1843 and it was adopted by Liebig and by almost all chemists. With the development of organic chemistry, however, it began to be apparent that there was to be a return to the law of volumes which had been completely sacrificed in the tables of Gmelin. This was first seen by Gerhardt and he brought most influential support to the system of Berzelius, at the same time introducing much needed corrections. His first and most important follower was Laurent.

Cannizzaro's Views.

In 1858, Cannizzaro proposed the doubling of many of the atomic weights to bring them into harmony with the theory of Avogadro and the law of specific heats. He insisted on a clear distinction being maintained between atoms and molecules and, with this distinction kept in view, the difficulties in the way of the acceptance of the theory of Avogadro disappeared. His views were based upon the work and conceptions of Avogadro, Regnault and Gerhardt. The theory of Avogadro, if true, must be the surest means of deciding upon the atomic weights. These views of Cannizzaro were given in his course of lectures and in the form of a letter to his colleague, Luca, professor of chemistry at Pisa.

Congress of Carlsruhe.

In 1860, a congress of chemists was called at Carlsruhe to put an end to the confusion and discord which existed between the diverse systems. Dumas presided. He accepted the atomic weights of Berzelius with modifications indicated by Regnault and Rose and Marignac, but opposed the introduction of the hypothesis of Avogadro. And yet in 1826 Dumas had published an important memoir, "Sur quelques points de la theorie atomistique" in which he had taken as his starting-point the theory of Avogadro in his search for a means of harmonizing the deductions from specific heats and isomorphism. This work had so impressed Cannizzaro that he had called it the theory of Avogadro, Ampere and Dumas. Hence his surprise was great at this opposition of Dumas, but so strong was the prestige and influence of Dumas that the congress reached no agreement. As Cannizzaro says,[1] the delegates separated without having passed any resolution and each one persisting in his opinion. Attention had been called, however, to the work of Cannizzaro and in a few years his conclusions were accepted by the majority of chemists. The change thus introduced in the atomic weights made the discovery of the Periodic Law possible.

Later Progress.

Since then the theoretical principles observed in atomic weight determinations have remained the same. The theory of Avogadro has approved itself as of the greatest value, the specific heats have been repeatedly appealed to, and less often the testimony of isomorphism. Improved analytical methods have introduced the greater number of changes, though much is still needed along this line. A fuller knowledge of the chemical behavior and analogies of the elements has brought about a number of corrections, the greatest help along this line coming through the discovery of the Periodic Law, an account of which is to follow in the next chapter.

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[1] "Les Actualites chimiques," II, 12.

Each of the later decades of the 19th century has seen steady improvement until, from a condition of great confusion and wide variation, a fair uniformity has been attained in the atomic weights accepted by chemists of all nationalities. The differences are now mainly due to differences in judgment as to the relative value of experimental determinations coming from various sources. Entire unanimity can only be attained by agreement between representatives of the great national societies of chemists. Such unanimity, however, must not be mistaken for actual approximation to the truth. Unquestionably a considerable number of the atomic weights still rest upon very slim evidence and much careful work is still needed.

Standard for the Atomic Weights.

The so-called atomic weights are, of course, not absolute but relative. They are after all to be considered as combining weights, and for purposes of comparison a standard is necessary. The discussion as to the best available standard has been going on for nearly a century. This has little bearing upon theory and is chiefly interesting because of its practical application in calculations. It is not necessary then to go into an extended historical account of the discussion. A brief résumé will be sufficient.

The Dalton Standard.

For the first table of atomic weights as given by Dalton, hydrogen was taken as the standard and 1 was the value assigned to it. This choice was doubtless determined by the belief that the hydrogen atom was the lightest and therefore all the other atomic weights would be represented by figures greater than unity.

The choice was confirmed by the hypothesis which soon arose that hydrogen was possibly the component of the other atoms. This was seen in Dalton's own work and in the hypothesis of Prout, which received wide credence and which has stubbornly resisted dislodgment from the minds of influential chemists. Hydrogen is therefore to be known as the Dalton standard.

Berzelian Standard.

The clear vision of Berzelius, to whom chemists are so largely indebted for the sure and safe foundation of their science, soon saw that more important reasons were to be considered than mere convenience or a sentimental regard for a unit standard. Above all things accuracy was demanded in these constants on which chemical work and chemical theory were to rest. The atomic weights represented ratios to the standard. All error could not be avoided in the experimental determinations of these ratios, but the error would be simple and not duplicated where the ratio was directly determined. Therefore that element should be taken as the standard which gave direct ratios with the largest number of elements. Under this provision but one element could be chosen, namely oxygen. Should any other element, as hydrogen, be chosen, then the ratio of this element to oxygen, as well as the ratio of oxygen to the element in question, would have to be determined and thus the error in the latter multiplied by the error in the former determination. However often the oxygen-hydrogen ratio may be revised, error is inevitable. It is a simple ordinary precaution against error, therefore, to discard the unnecessary use of the oxygen-hydrogen ratio and to take the direct ratio as final. It may be added that hydrogen would be an especially poor choice for the direct ratios as less than half a dozen such have been satisfactorily determined. If the error in the oxygen-hydrogen ratio be supposed to be only 0.1 per cent., and this is really less than the probability, then we would have an error of over 1 per cent. in many of the higher atomic weights apart from the error due to experiment.

The necessity then for choosing oxygen as the standard could not fail to impress itself upon so clear-sighted a chemist as Berzelius, and it would be a further recommendation to his mind that the oxygen standard would be a protest against the wild hypothesis of Prout. The hydrogen standard was, however, preferred by many chemists and was the only one in common use during the greater part of the 19th century.

The Value Assigned the Standard.

Due consideration of the points mentioned above have convinced the majority of chemists of the present day that the proper standard is oxygen. It only remains to assign it a value. Some have contended that a standard must be the unit also. This is a custom which has been departed from in many cases and need not be binding upon chemists if it involves inconveniences and inaccuracies. The adoption of the value 1 or 10 for oxygen would involve the use of fractional atomic weights for some elements. Wollaston used the value 10 for oxygen but had little following. Berzelius used the value 100 for oxygen. This gives us a large number of atomic weights of inconvenient size. Roughly speaking, all of the atomic weights at present in use would have to be multiplied by 6 ¼. A number of them therefore would lie between 1200 and 1500. This probably accounts for Berzelius' lack of success in establishing oxygen as the standard. Seeing that the hydrogen unit predominated during most of the 19th century, and that for the greater part of this time oxygen was rounded off into the whole number 16, and for the remainder varied very little from this figure, it is evident that the value of the literature of this period will be least impaired by the adoption of oxygen as 16. The labor of learning a new table and of converting the old data into the new system would be both burdensome and distasteful if any other number were chosen. At the same time this is the smallest number which can be assigned oxygen, still keeping all other atomic weights greater than unity.

The discussion has been a prolonged one and is not entirely settled yet, although the first century of the atomic weights will soon draw to its close. The discussion is not as to the theory but involves such simple questions that it should have been satisfactorily settled long ago.

CHAPTER V.

The Periodic or Natural System.

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THE PERIODIC OR NATURAL SYSTEM.

The grouping together of chemical bodies according to certain observed analogies, was attempted before elements were distinguished from compounds, and, as has been pointed out, numerical relationships were suggested between combining equivalents before the new atomic theory had been formulated. Such relationships then need not have any bearing upon the question of the atoms which forms our immediate study. But very soon after Dalton's announcement of the atomic theory some of these relationships were regarded as revealing the possibly composite nature of the elementary atoms, and from the study of these regularities and analogies there has been gradually unfolded that which has been called the Periodic System of the Elements, but for which the name Natural System, first assigned to it, might with great advantage be again adopted.

The discovery of this Natural System has done so much to make clearer the nature of the atom that a careful study of its development and characteristics is most essential. Very little space need be given to the many efforts at discovering numerical regularities between the atomic weights, as they have thrown little light upon the atom, and have not succeeded in proving its divisibility nor composite nature. Most of the regularities require the acceptance of approximations instead of rigidly adhering to actually determined numbers; many of the deductions have little basis, and the simple arithmetical probability of many such regularities occurring between any 70 numbers chosen at random, ranging from 1 to 240, does not seem to have been taken into account.

Historically, the most noted of these regularities is that which has become famous as Prout's hypothesis.

Prout's Hypothesis.

In 1815,[1] in a paper upon the relations between the specific gravities of bodies in the gaseous state and their atomic weights, Prout stated that he had often observed the near approach to round numbers of many of the weights of the atoms. From the table at his command he further deduced that all elementary numbers, hydrogen being considered as 1, are divisible by 4, except carbon, nitrogen and barium, and these are divisible by 2, appearing, therefore, to indicate that they are modified by a higher number than unity or hydrogen. He thought the other number might be 16 or oxygen, and that possibly all substances were composed of these two elements.

Later, in 1816,[2] he expressed the following views: "If the views we have ventured to advance be correct, we may almost consider the *πρώτη ὕλη* of the ancients to be realized in hydrogen, an opinion, by-the-by, not altogether new. If we actually consider this to be the case, and further consider the specific gravities of bodies in their gaseous states to represent the number of volumes condensed into one, or, in other words, the number of the absolute weights of a single volume of the first matter (*πρώτη ὕλη*) which they contain, which is extremely probable, multiples in weight must always indicate multiples in volume and *vice versa*, and the specific gravities or absolute weights of all bodies in a gaseous state must be multiples of the specific gravity or absolute weight of the first matter, because all bodies in a gaseous state, which unite with one another, unite with reference to this volume."

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[1] *Ann. Phil.*, Thomsen, 1815, **11**, 321.

[2] *Ann. Phil.*, Thomsen, 1816, **12**, 111.

Berzelius' Antagonism.

Now this is all of the evidence and the only argument which has ever been adduced in favor of this hypothesis. And yet the fascinating dream, a kind of renascence of the Pythagorean belief in the unity of matter, was pursued as an *ignis fatuus* throughout the 19th century. Several times it was thought to have been disproved and the question satisfactorily settled, but after a brief disappearance it came forth again, sometimes in a modified form and with new followers. Its first and strongest antagonist was Berzelius who, however, had regarded it with favor when first brought to his notice. In 1825 he published a table of the atomic weights which contained a number of fractions, and he protested very strongly against the practice of rounding off these fractions into whole numbers. As Hoffman says, "He could not persuade himself that the numerical relations of these values betokened an inner connection of the elements nor yet a common origin. On the contrary, he was of the opinion that these apparent relations would disappear more and more as these values were more accurately determined. For him, therefore, there existed as many forms of matter as there were elements: in his eyes the molecules of the various elements had nothing in common with one another save their immutability and their eternal existence." Our later knowledge of these matters would seem to show that in this Berzelius had gone too far to the other extreme.

Fate of the Hypothesis.

In 1832 Turner was specially delegated by the British Association to investigate this question. If barium, chlorine, etc., really had fractional atomic weights, then the hypothesis in its original form was untenable. Turner's results were adverse to it. So also were Penny's. Marignac suggested that if half the atomic weight of hydrogen were taken, then all known atomic weights would be practically multiples of it. The idea was taken up by Dumas with enthusiasm, but he found this factor must be once more halved and thus one-fourth the hydrogen atom taken. It is not quite clear why this is not a begging and abandonment of the whole question. But the very careful and accurate work of Stas upon the atomic weights made even this position impossible. When Zängerle[1] extended the hypothesis to the 0.001 part of the hydrogen atom it passed the limit of all experimental evidence and lost all weight and meaning. Accurate determinations have shown that while certain of the atomic weights approximate closely to whole numbers, others usually do not. The hydrogen atom cannot be contained in them an even number of times. Any fraction whatever of the weight of the hydrogen atom cannot be considered without abandoning the fundamental idea of an atom and such consideration can have no clear meaning nor be of any true value.

Numerical Regularities.

There have been a number of attempts at discovering some mathematical formula by means of which atomic weights might be calculated or interpolated in a series. Thus there was the equation of Cooke[2] elaborated still further by Dumas[3]; the logarithmic expression of Johnstone Stoney[4]; the algebraic expression of Carnelley[5], and others equally futile. This truth is made apparent by the most accurate determinations that these atomic

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[1] *Ber. d. chem. Ges.*, **4**, 570-574.

[2] *Am. J. Sci.*, [2], **17**, 387.

[3] *Compt. Rend.*, **45**, 709; **46**, 951; **47**, 1026.

[4] *Chem. News*, **57**, 163.

[5] *Phil. Mag.* (5), **29**, 97-115.

weights do not form a regular series but a most irregular one, the gradations from one to the other varying too greatly to meet the requirements of any mathematical expression. If there is any deeper meaning in the great number of numerical regularities observed it has not been discovered.

Deobereiner's Triads.

The first classification of the elements depending upon the atomic weights was through what were known as the Triads of Döbereiner. This chemist seems to have observed[1] first that the combining weight of strontium was the arithmetical mean of those of calcium and barium. This was in 1816, and the accepted numbers at that time were 27.5 for calcium, 72.5 for barium and 50 for strontium. This led him for a while to question the independent existence of strontium. After the publication in 1825 of the more accurate table of atomic weights by Berzelius, the matter was brought up again by Döbereiner. Several such triads were mentioned, as lithium, sodium, and potassium; chlorine, bromine and iodine; sulphur, selenium, and tellurium. He was careful not to let this grouping depend upon the atomic weights alone but insisted that only elements exhibiting decided analogies of properties must be considered together. Thus the fact that nitrogen was the mean between carbon and oxygen could not be held as meaning anything since no analogy existed between them. Such warning was most clearly needed for it is evident that wherever the atomic weight of an element happened to be equidistant from any other two it would form the arithmetic mean. Of course there would be a large number of such groups. It is evident that to generalize on this slight evidence so as to deduce

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[1] *Ann. d. phys.*, **56**, 332.

a supposed law that the elements occurred in groups of threes, is going to an unwarranted length, yet this seems to be the assumption. It was taken up by other chemists, notably by Gmelin in his "Handbook," and many analogies and groups were sought for. Then for a number of years little attention was paid to these triads. In 1857, however, Lennsen[1] returned to this doctrine of triads, endeavoring to force all of the elements into some twenty such groups. Then Odling[2] endeavored to build upon them an elaborate system of the elements which he called the Natural System. The system was also based on a consideration of all known properties as well as the atomic weights. It was too artificial and faulty to receive much attention.

These triads of elements can still be seen in the more perfect system of to-day, but the interpretation of the phenomenon is as far off as ever. It should be noted that the fact that the atomic weight is the arithmetical mean of those of two other analogous elements, carries with it often the further phenomenon that the other properties are arithmetical means also. In this we can only see one of the fundamental propositions of the periodic system.

Gladstone's Ascending Series.

The first to suggest an arrangement of the elements in the order of their atomic weights was Gladstone.[3] This was in 1853 and he made use of the faulty and imperfect table of weights given in Liebig's *Jahresberichte* for 1851. Thus the atomic weights of metals analogous to iron were halved. This threw a large number of elements as aluminum, silicon, chromium,

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[1] *Ann. Chem. Pharm.*, **103**, 121.

[2] *Phil. Mag.*, [3], **13**, 423.

[3] *Phil. Mag.*, [4], **5**, 313.

manganese, iron, cobalt and nickel between the numbers 27 and 29. This and other groups having nearly the same atomic weight for a number of elements attracted the attention of Gladstone and misled him, obscuring the natural system of the elements. It is not surprising then that his Ascending Series received little notice.

Homologous Series.

Several ingenious observations and suggestions were made during this period immediately preceding the introduction of the revised atomic weights. Thus Pettenkofer[1] compared the elements with the compound radicals of organic chemistry and suggested that they might be looked at from the same standpoint. Later, Dumas,[2] making use of the formula devised by Cooke, tried to reproduce with the elements homologous series similar to those of the organic radicals. Later still, there were one or two efforts at arranging the elements according to the lately discovered property of valence.

Telluric Screw.

The first use of the revised atomic weights in an ascending series was by De Chancourtois,[3] and though his work lay unnoticed for thirty years, it contained much of the Periodic Law. He drew as a conclusion from his work that: "Les propriétés des corps sont les propriétés des nombres."

The fundamental idea of the Telluric Screw consisted in writing the values of the atomic weights along the generatrix of a vertical cylinder, the circular base of which was divided into 16 equal parts, 16 being the atomic weight of oxygen. If we then trace upon the cylinder a helix with an angle of 45° to its axis, each point of the helix

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[1] *Ann. Chem. Pharm.*, **105**, 188.

[2] *Compt. rend.*, **45**, 709.

[3] "Vis Tellurique," Paris, 1863.

may be considered as the characteristic point of a simple body, the atomic weight of which, proportional to the corresponding length of the spiral, will be read upon the generatrix which passes by this point. At each turn, the helix returns on one and the same perpendicular at distances from the summit of the cylinder, which are multiples of 16, and mark the bodies whose atomic weights conform to this condition. In the same manner the various points of intersection of the helix with any of the sixteen principal generatrices, traced from the divisions of the circular base, correspond to elements whose atomic weights differ among themselves by 16 or a multiple of 16.

We have in this arrangement evidences of the influence of Dumas, especially in the emphasis laid upon the numbers 8 and 16. It is manifest also that De Chancourtois started out with the idea that the differences between the atomic weights ought to be constant. Gaps were filled out by imagining new varieties of known simple bodies which he called Secondary Characters. Analogies were forced, and there were other faults which prevented a wide consideration or acceptance of the arrangement.

Law of Octaves.

In the work of Newlands,[1] which followed closely upon that of De Chancourtois, we we have a nearer approach to the Natural System. He too arranged the elements in an ascending series according to their atomic weights. Numbering these elements 1, 2, 3, etc., he observed that the difference between the number of the lowest member of a group and that immediately above it is 7; in other words, the eighth element starting from a given one is a kind of repetition of the first, like the eighth note in music. But then he lost his grasp of the system, maintaining that the differences between the numbers of the other members of

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[1] *Chem. News*, **10**, 94.

a group are frequently twice as great; thus in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic 13; between arsenic and antimony 14; and between antimony and bismuth 14. The truth is, the list of atomic weights was still too imperfectly filled out for the system to appear clearly, or for one to grasp it, unless furnished with a wide knowledge of chemical facts.

A year later[1] Newlands had still further worked out his idea, giving his discovery the name of "a law." In his new table which is here reproduced, he transposed some of the elements so as to bring them into their proper groups. Arranging his table in a vertical series, he observed that elements belonging to the same group usually appear on the same horizontal line. In order to allow for certain elements which had their atomic weights very close together, as cobalt and nickel, Newlands modified his law thus: "The numbers of analogous elements *when not consecutive* differ by 7 or by some multiple of 7."

NEWLAND'S TABLE OF OCTAVES (1866).

	No.		No.		No.		No.
H	1	F	8	Cl	15	Co and Ni	22
Li	2	Na	9	K	16	Cu	23
G	3	Mg	10	Ca	17	Zn	24
Bo	4	Al	11	Cr	18	Y	25
C	5	Si	12	Ti	19	In	26
N	6	P	13	Mn	20	As	27
O	7	S	14	Fe	21	Se	28
Br	29	Pd	36	Te	43	Pt and Ir	50
Rb	30	Ag	37	Cs	44	Os	51
Sr	31	Cd	38	Ba and V	45	Hg	52
Ce and La	32	U	39	Ta	46	Tl	53
Zr	33	Sn	40	W	47	Pb	54
Di and Neo	34	Sb	41	Nb	48	Bi	55
Ro and Ru	35	I	42	Au	49	Th	56

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[1] *Chem. News*, **12**, 83.

Hinrichs on the Properties.

In 1866 Hinrichs[1] deduced from his observations on the spectra of elements the important fact that the properties of the chemical elements are functions of their atomic weights. This was three years before the announcement of Mendeléeff and the modes of expression are almost identical.

Meyer's Table.

The name of Lothar Meyer has been very commonly associated with the development of the Periodic or natural system. His first table was given in 1864 in the first edition of his work "Die modernen Theorien der Chemie." The table was as follows:

MEYER'S FIRST TABLE, 1864.

4 Val.	3 Val.	2 Val.	1 Val.	1 Val.	2 Val.
....	....	....	....	Li... 7.03	(Be .. 9.3)
Diff.	....	....	....	16.02	(14.7)
C .. 12.0	N .. 14.04	O .. 16.00	F .. 19.0	Na .. 23.05	Mg .. 24.0
Diff. 16.5	16.96	16.07	16.46	16.08	16.0
Si .. 28.5	P .. 31.0	S .. 32.0	Cl . 35.46	K... 39.13	Ca .. 40.0
Diff. 44.45	44.0	46.7	44.51	46.3	47.0
....	As . 75.0	Sc . 78.8	Br . 79.97	Rb .. 85.4	Sr... 87.0
Diff. 44.55	45.6	49.5	46.8	47.6	49.0
Sn . 117.6	Sb . 120.6	Te . 128.3	I... 126.8	Cs .. 133.0	....
Diff. 44.7	43.7	....	....	35.5	....
Pb . 207.0	Bi .. 208.0	....	....	Te. (204.0)	Ba... 137.1

4 Val.	4 Val.	4 Val.	2 Val.	1 Val.
Mn. 55.1	Ni .. 58.7	Co. 58.7	Tn. 65.0	Cn .. 63.5
Fe . 56.0	....	....	....	....
Diff. 49.2 48.3	45.6	47.3	46.9	44.4
Rn . 104.3	Rh . 104.3	Pd. 106.0	Cd. 111.9	Ag . 107.94
Diff. 46.0	46.4	46.5	44.5	44.4
Pt .. 197.1	Ir .. 197.1	Os . 199.0	Hg 200.2	An . 196.7

[1] *Am. J. Sci.*, **32**, 350.

The elements are arranged horizontally in the sequence of their atomic weights to a certain extent, but a number of elements as copper, silver, gold, and others, were excluded from their proper sequence. It is clear from a closer study of the table that the idea of the natural families, already well known, was the predominant one and that the numerical order of the atomic weights was subordinated to it. Thus the four first elements form a series, and the others are in sixes. Some elements are omitted and vacant spaces are left in other cases. In the fourth series, we have the first member omitted in order that analogous elements may fall properly. There is less evidence of periodicity than in the table of Newlands.

His incomplete table, as handed to Remele in 1868[1], is but a slight improvement over the earlier table and still shows only a groping after the cardinal principles of the system, namely, the orderly sequence of the weights and the periodicity of the elements. Later, in 1870, one year after the publication of Mendeléeff's table, Meyer gave a third table in which the order of the 1864 table is reversed, the sequence falling in vertical lines instead of horizontal. This latter table indeed bears scant resemblance to either of the earlier ones. As Meyer had seen an abstract of Mendeléeff's article before the publication of his, he stated later that he claimed credit only for points in which he thought he had improved upon that table. Taking all into consideration, it is difficult to fix upon any important contribution of Meyer to the discovery of the Periodic Law.

Table of Mendeleeff.

The first table published by Mendeléeff[2] is one with a vertical arrangement according to atomic weights, a second ta-

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[1] *Ztschr. anorg. Chem.*, 9, 354.

[2] *J. Russ. Chem. Soc.*, 1869, p. 90.

ble, however, accompanying it, which showed much more clearly the natural system. The first gave all the elements, with blank spaces for four unkown elements. It failed very decidedly to show the natural families of elements except in the case of a few well-known ones. The table is here given :

Mendeléeff's Table, 1869.

			Ti..... 50	Zr .. 90	? 180
			V..... 51	Nb.. 94	Ta.. 182
			Cr 52	Mo . 96	W .. 186
			Mn ... 55	Rh.. 104.4	Pt .. 197.4
			Fe 56	Ru.. 104.4	Ir... 198
			NiCo.. 59	Pd .. 106.6	Os.. 199
H.. 1			Cu.... 63.4	Ag .. 108	Hg.. 200
	Be.. 9.4	Mg.. 24	Zn.... 65.2	Cd.. 112	
	B... 11	Al .. 27.4	? 68	Ur .. 116	Au.. 197
	C... 12	Si .. 28	? 70	Sn .. 118	
	N .. 14	P... 31	As 75	Sb .. 122	Bi .. 210
	O... 16	S... 32	Se 79	Te .. 128	
	F... 19	Cl .. 35.5	Br 80	I.... 127	
	Na.. 23	K... 39	Rb.... 85.4	Cs .. 133	Tl .. 204
		Ca .. 40	Sr 87.0	Ba .. 137	Pb.. 207
		? 45	Ce 92		
		? 56	La 94		
		? 60	Di 95		
		? 75.6	Th.... 118		

The second table did not include all of the elements and had many blank spaces. Evidently the author was very seriously handicapped by the imperfect knowledge of a large number of elements then at his command. Nothing can better illustrate the immense service which this system has been to the science of chemistry than the increase in knowledge of these elements and their comparative properties since that time. Much of this increase can be directly traced to the influence of this great discovery.

MENDELÉEFF'S SECOND TABLE.

Li	Na	K	Cu	Rb	Ag	Cs	..	Tl
Be	Mg	Ca	Zn	Sr	Cd	Ba	..	Pb
B	Al	..	..	..	Ur	..	..	Bi
C	Si	Ti	..	Zr	Sn	..	..	..
N	P	V	As	Nb	Sb	..	Ta	..
O	S	..	Se	..	Te	..	W	..
F	Cl	..	Br	..	I	..	..	..

It required an insight into the principles of the natural system to devise this latter table, and the conclusions reached by Mendeléeff in this first paper give proof that he had grasped these principles. The most important of these were :

1. The elements, if arranged according to their atomic weights, exhibit an evident periodicity of properties.

2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value or which increase regularly.

3. The arrangement of the elements, in the order of their atomic weights, corresponds to their so-called valences, as well as, to some extent, to their distinctive chemical properties.

4. The elements which are most widely diffused have small atomic weights.

5. The magnitude of the atomic weight determines the character of the element just as the magnitude of the molecule determines the character of a compound body.

Two years later he gave a table which is practically the same in form as the one in use at the present day.

Mendeléeff especially emphasized the idea of periodicity. Afterwards he said :[1] "The repetition of the word periodicity shows that from the very beginning I held this to be the fundamental property of my system of the ele-

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[1] *Ber. d. chem. Ges.*, **13**, 1796.

Mendeléeff's Table, 1871.

Series.	Group I. R_2O.	Group II. RO.	Group III. R_2O_3.	Group IV. RH_4. RO_2.	Group V. RH_3. R_2O_5.	Group VI. RH_2. RO_3.	Group VII. RH. R_2O_7.	Group VIII. RO_4.
1	**H**=1							
2	**Li**=7	**Be**=9.4	**B**=11	**C**=12	**N**=14	**O**=16	**F**=19	
3	**Na**=23	**Mg**=24	**Al**=27.3	**Si**=28	**P**=31	**S**=32	**Cl**=35·5	
4	**K**=39	**Ca**=40	—=44	**Ti**=48	**V**=51	**Cr**=52	**Mn**=55	**Fe**=56, **Co**=59 **Ni**=59, **Cu**=63
5	(**Cu**=63)	**Zn**=65	—=68	—=72	**As**=75	**Se**=78	**Br**=80	
6	**Rb**=85	**Sr**=87	?**Y**=88	**Zr**=90	**Nb**=94	**Mo**=96	—=100	**Ru**=104, **Rh**=104 **Pd**=106, **Ag**=108
7	(**Ag**=108)	**Cd**=112	**In**=113	**Sn**=118	**Sb**=122	**Te**=125	**I**=127	
8	**Cs**=133	**Ba**=137	?**Di**=138	?**Ce**=140	....	....	....	....
9	....	....	....	....	....	...	....	....
10	...	....	?**Er**=178	?**La**=180	**Ta**=182	**W**=184	....	**Os**=195, **In**=197 **Pt**=198, **Au**=199
11	(**Au**=199)	**Hg**=200	**Tl**=204	**Pb**=207	**Bi**=208	....	....	
12	....	....	....	**Th**=231	....	**U**=240	....	....

ments.'' Further, he maintained that the system can be arranged in the form of a spiral and in this the resemblances appear among the members of every other series. Mendeléeff devoted great energy and wide chemical knowledge to the filling out of his great discovery, and the credit for the expansion and filling out of the system, and the bringing of various compounds of the elements into consideration also has been largely due to his skill and knowledge.

Basis of a Natural System.

It is evident that any classification of the elements which purports to be in accord with nature, or a natural system, cannot have an arbitrary basis, but must be on one or more of the properties of the elements. It is conceivable that the selection of different properties as bases might lead to varying systems. The Periodic System deserves the name of the Natural System *par excellence* because it is not based on one but all of the properties of the elements. There were a number of efforts at classifying these elements before the discovery of this system, but all were unsatisfactory. Thus the division into metals and non-metals, or, as they were called, metalloids, was in the main based upon the electrochemical character. The division into artiads and perissads depended upon the valence. A more common grouping was into families of analogous elements. Here analogies of properties in general were made use of. This enabled a few strongly marked groups to be distinguished, but a large number of the elements could not thus be grouped and the system was only a partial one and not a complete classification. A proper classification conduces greatly to systematic and successful study, and the lack of this accounts for the slow development of inorganic chemistry before the announcement of the Periodic System.

Periodicity of Properties. On examining the periods of elements obtained by arranging them in an ascending series according to their atomic weights it is readily seen that this accords with the electrochemical properties also, for each period begins with a positive element and the positive character diminishes until at the end of each period is a negative element. In these periods again, the valence in regard to hydrogen increases regularly up to the fourth member, and then regularly diminishes until the seventh member is reached. The oxygen-valence increases regularly from the first to the seventh member. Similar gradations are noted in the case of other properties such as specific gravity, specific heat, solubility, melting-point, etc. Thus this natural system should be looked upon as based upon a consideration of all the properties and not upon the weight of the atomic masses alone. This point of view is an important one and should be borne in mind. The same arrangement could have been arrived at, independent of the atomic weights, by a consideration of the valence or electrochemical character alone.

Graphic Representation. It is very important for the study and proper grasping of the periodic system that a suitable graphic representation of it be devised. There have been many attempts at doing this, most of which have failed and none of which have proved entirely satisfactory. There are certain essential points to be considered in devising any such graphic table. First, the periods must be properly given. These may be looked upon as periods of 7 with periods of 3 occurring at intervals. Some have chosen to consider them as periods of 7 and 17. Again, the analogies of the elements must be kept in mind and should appear clearly in the scheme. Then the differences between the atomic weights of the elements in the ascending series must be considered. These may be called the atomic weight differences. Lastly, the distances between the periods, that is, the differences between the atomic weights of analogous elements in adjoining periods, have an important bearing upon the arrangement. It must be borne in mind that the atomic weight differences and the period distances are far from uniform. The first have a range from 1 to 6 or more, and the latter from 15 to 51 or possibly 91. This has been lost sight of by many who have grappled with the problem. It should be perfectly clear that it renders any tracing of a regular curve absolutely impossible. Many, as de Chancourtois,[1] Meyer,[2] Baumhauer,[3] Huth[4] and others have fancied the spiral arrangement or that of a helix. Indeed Mendeléeff suggested this also. No spiral can be devised, however, Archimedean, logarithmic or of any other character, which will allow for the irregularities in both atomic weight differences and period distances. All who attempted a spiral representation have disregarded this lack of uniformity and rested content with crude approximations which cannot be tolerated. If such a mathematical curve could be drawn, manifestly the equation to it would give a simple and easy method of calculating any and all atomic weights with great accuracy. In spite of exhaustive search, such an equation has never been found and such calculations have not proved possible.

[1] *Loc. cit.*

[2] Meyer: "Mod. Theorien d. Chemie."

[3] "Bez. zwisch. d. Atomgew." Braunschweig, 1870.

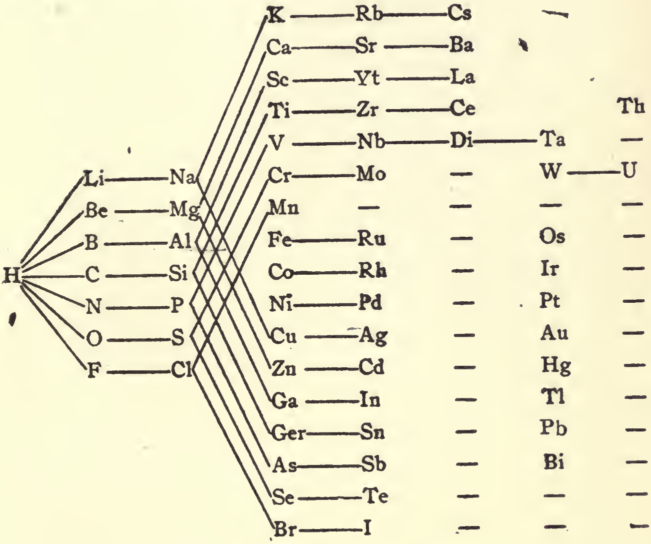
[4] "Period. Gesetz d. Atomgew.," Frankfurt, 1884.

Three tables have been given which have been more or less used and which present points of advantage over most others. These tables follow:

TABLE OF LOTHAR MEYER.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
Li 7.08	Be 9.08	B 10.9	C 11.97	N 14.01	O 15.96	F 19.06			
Na 22.99	Mg 23.94	Al 27.04	Si 28	P 30.96	S 31.98	Cl 35.37			
K 39.03	Ca 39.91	Sc 43.97	Ti 48	V 51.1	Cr 52.45	Mn 54.8	Fe 55.86	Co 58.6	Ni 58.6
Cu 63.18	Zn 64.88	Ga 69.9	Ger 72	As 74.9	Se 78.87	Br 79.76			
Rb 85.2	Sr 87.3	Y 89.6	Zr 90.4	Nb 93.7	Mo 95.9	? 99	Ru 103.5	Rh 104.1	Pd 106.2
Ag 107.66	Cd 111.7	In 113.4	Sn 117.35	Sb 119.6	Te 126.3	I 126.54			
Cs 132.7	Ba 136.86	La 138.5	Ce 141.2	Di 145	? 151	? 152			
? 165	? 170	Yb 172.6	? 176	Ta 182	W 183.6	? 185	Os 191	Ir 193.5	Pt 194.3
Au 196.2	Hg 199.8	Tl 203.7	Pb 206.39	Bi 207.5	? 210	? 211			
? 222	? 226	? 230	Th. 231.96	? 234	Ur 239.8				

BAYLEY'S TABLE, 1882.



			K	Rb	Cs	—	
			Ca	Sr	Ba		
			Sc	Yt	La		
			Ti	Zr	Ce		Th
			V	Nb	Di	Ta	—
	Li	Na	Cr	Mo	—	W	U
	Be	Mg	Mn	—	—	—	—
	B	Al	Fe	Ru	—	Os	—
H	C	Si	Co	Rh	—	Ir	—
	N	P	Ni	Pd	—	Pt	—
	O	S	Cu	Ag	—	Au	—
	F	Cl	Zn	Cd	—	Hg	—
			Ga	In	—	Tl	—
			Ger	Sn	—	Pb	—
			As	Sb	—	Bi	—
			Se	Te	—	—	—
			Br	I	—	—	—

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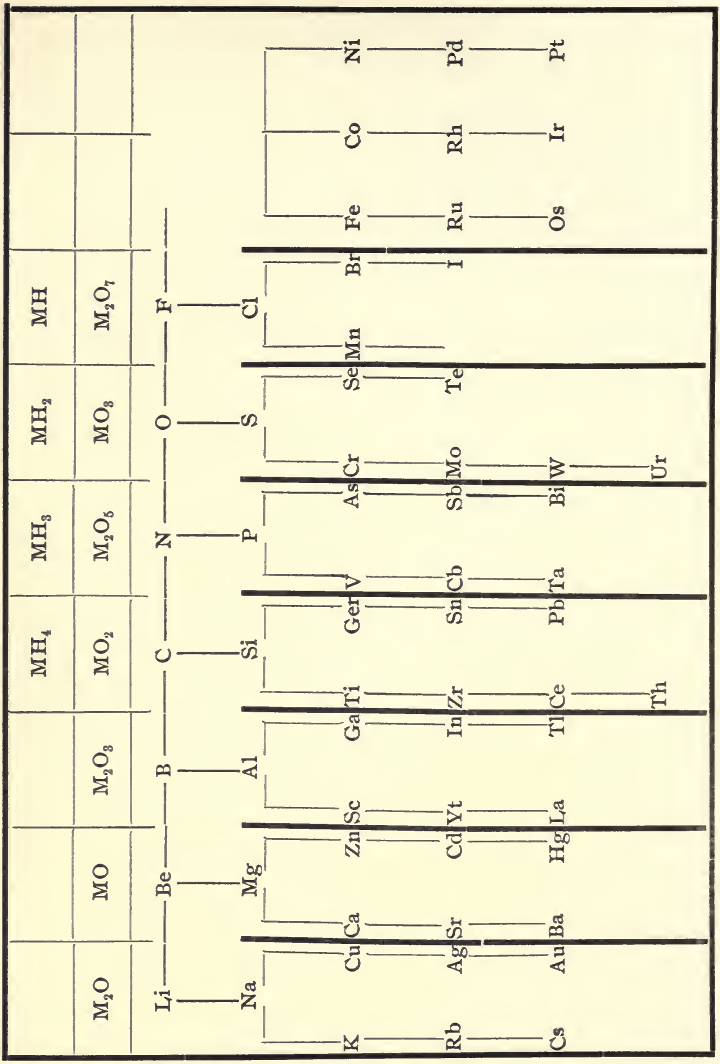
[1] *Phil. Mag.*, (5), **13**, 26.

VENABLE'S TABLE,[1] 1895.



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[1] *J. Am. Chem. Soc.*, **17**, 75.

Analogies of the Elements. The closer study of the system has shown that the elements of the first period present many analogies. Thus lithium approaches beryllium in many of the characteristics, boron resembles carbon so much that in earlier classifications it was placed in the same family. The characteristics of the group appear more distinctly in the elements of the second period. Thus sodium is more typically an alkali than lithium, magnesium more representative of its group than oxygen, phosphorus more of its group than nitrogen, etc. It would seem that the groups diverged more and more in their properties as the atomic weights increased, or as they got further away from some common origin. The cross analogies are prominent in the first period, but less so in the second, and hence have less effect in modifying the development of the peculiar characters of that group. From the second period on we have the recurrence of periods of 17, or rather double periods of 7 with an intermediate 3. This gives in each column or group two series presenting analogies, and yet striking differences. This was called by Meyer "double periodicity," by Mendeléeff "matched and unmatched series." A close study will show that both series show points in common with the elements of the second period. Thus both potassium and copper resemble sodium; calcium and zinc resemble magnesium, and much more than they resemble one another, etc. This is only slightly indicated in Mendeléeff's arrangement. One series is placed beside the other and a little lower. An examination of the latter two tables will reveal that both give a better comprehension of the facts mentioned above than does the table of Mendeléeff. Thus, taking the last one, the group elements are those of the first period. The type elements are those of the second, and from them branch the right and left series. On the positive side of the table the left-hand series show greater analogies to the type. On the negative side the elements of the right-hand series resemble the type more closely.

Periodicity of the Elements.

The periodicity of the elements may be seen from the following examples: Taking the members of the second horizontal series the oxides and hydroxides progress regularly from left to right: Na_2O, Mg_2O_2 (MgO), Al_2O_3, Si_2O_4 (SiO_2), P_2O_5, S_2O_6 (SO_3), Cl_2O_7.

$NaOH$, $Mg(OH)_2$, $Al(OH)_3$, $Si(OH)_4$, $PO(OH)_3$, $SO_2(OH)_2$, $ClO_3(OH)$.

So too the chlorides: $NaCl$, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5, S_2Cl_4, ICl_3.

Taking the physical properties for the same series:

	Na.	Mg.	Al.	Si.	P.	S.	Cl.
Spec. Grav...	0.97	1.75	2.67	2.49	1.84	2.06	1.33
Atom. Vol ...	24	14	10	11	16	16	27
	NaO	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Spec. Grav...	2.8	3.7	4.0	2.6	2.7	1.9	?
Atom. Vol ...	22	22	25	45	55	82	?

Again, if we take the first two vertical groups we find the atomic weights, specific gravities, atomic volumes and specific heats show a peculiar dependence upon or relationship to one another.

Li.	**Be.**
7.02	9.0
0.59	1.64
11.9	7.0
0.9408	0.4702
Na.	**Mg.**
23.05	24.3
0.97	1.743
23.5	13.95
0.2934	0.245

K.	**Cu.**	**Ca.**	**Zn.**
39.11	63.6	40.	65.3
0.865	8.8	1.58	7.2
44.88	7.0	25.6	9.04
0.166	0.095	0.1686	0.095
Rb.	**Ag.**	**Sr.**	**Cd.**
85.5	107.9	87.6	112.
1.52	10.5	2.54	8.65
56.4	10.3	33.9	12.69
0.073	0.055	0.074	0.056
Cs.	**Au.**	**Ba.**	**Hg.**
132.9	197.3	137.43	200.
1.88	19.5	3.75	14.19
70.68	10.24	36.54	14.12
0.047	0.035	0.046	0.031

Difficulties of the System.

The table of the Periodic System is incomplete. Between 60 and 70 elements have found places. More than 12 others are known and new ones are occasionally announced. The question naturally arises whether these will all fit into the vacant places in the table. More than 30 elements can be placed without changing the arrangement. The belief is justified that if the 60 odd known elements all drop into their proper order without difficulty, the remainder will also do so. It is mere idle juggling, however, to attempt to locate substances whose elementary nature is not positively proved, the atomic weights imperfectly known, and the properties and compounds practically unstudied. As the table is based upon all of the properties, and not the atomic weights alone, it has been urged with reason, that only elements that form compounds and obey the laws of affinity and valence can possibly enter into the table. It is readily conceivable that other elements may exist. Their masses would have weight but they might lack that property which would cause them to attract and be attracted by other bodies so as to unite with them in compounds. Of course, should they not be able to form compounds they could exhibit no valence. It would seem altogether incongruous to consider and classify such bodies among the active chemical elements, depending for their classification solely upon the weight of their masses. The fact that argon and its companions have been known for several years and all known methods used in vain for securing compounds of these bodies with known chemical elements would seem to indicate the possible existence of a different class of elements from those commonly so-called. This is a matter so important for all chemical theory, and of such deep interest that it seems strange that it has not been made the subject of exhaustive investigation instead of the somewhat desultory and unsatisfactory attacks upon the problem.

Position of Hydrogen.

One of the difficulties of the system is the proper placing of hydrogen. This has so far met with no adequate solution. With an atomic weight slightly greater than unity, this element forms the beginning of the ascending series. The next known element in the series is lithium with an atomic weight of 7.03, unless the inactive element helium (atomic weight 2.00) be considered. This would give an atomic weight difference of 6.022, which is about three times as great as the atomic weight differences for the first periods. Hydrogen will not fall in the lithium-fluorine period. It is possible that it may be the first element of a period between 1 and 7, helium falling in this period and 5 other unknown elements. This was suggested by Mendeléeff, and the idea has been elaborated by Reynolds and others. Some of the properties of hydrogen would ally it with the elements of the first group, as valence, electrochemical nature and the analogies of a number of compounds. The divergence in properties from the type of the group indicate that this sub-period would prove a very remarkable one.

The tables which give hydrogen as a primal element with lines radiating toward the elements of the first period assign it to a position unjustified by its properties and are based upon or lead to unwarranted assumptions as to the genesis of the elements. Hydrogen cannot be placed by properties in a position intermediate between lithium and fluorine. The only thing that is certain is that in the ascending series hydrogen must be left out of the count if the elements are to fall into analogous periods of seven.

Genesis of the Elements.

The consideration of the Periodic System has given rise to a number of suggestions as to the genesis of the elements, in spite of the protest of Mendeléeff who has maintained that the system had no bearing upon it and could not properly be used as a basis for any such speculations. It is true that the table of the elements does not give any positive knowledge as to their origin, nor even afford any very definite clue to aid in an investigation into this genesis, but it does reveal enough to lend some color to such speculations, and they have an added attraction from the unsolved problems connected with the system.

Certain deductions seem to be warranted, however. A study of the system cannot fail to convince one that a relationship exists between the elements. The idea held in the earlier part of the 19th century and voiced by Berzelius, that the elements are distinct and unrelated bodies, is no longer tenable. The kinship is in some way bound up with the atomic weight or mass, and with the gradation in atomic weight there is to be seen a gradual and proportional change in the relationship. Analogy in properties here can only mean analogy in nature and cannot be a chance coincidence, seeing that it is systematically shown. The inference is easily drawn, though of course it is merely a plausible guess, that these elements have a common origin or a common factor or factors. Some of the hypotheses as to the genesis of the elements are given here in order that the nature of these speculations may be seen. It must be borne in mind, that they do not form a part of chemical theory, and that they go far beyond the interpretation of observed facts.

Hypothesis of Crookes.

In a lecture before the British Association, Crookes[1] gave a hypothetical picture of the genesis of the elements. He supposed first the existence of a primal substance, called by him protyle, in an "ultra-gaseous state, at a temperature inconceivably hotter than anything now existing ; so high that the chemical atoms could not yet have been formed, being still far above their dissociation point. * * * But in course of time, a process akin to cooling, probably internal, reduces the temperature of the cosmic protyle to a point at which the first step in granulation takes place ; matter as we know it comes into existence and atoms are formed. * * * With the birth of atomic matter the various forms of energy which require matter to render them evident, begin to act ; and amongst others, that form of energy which has for one of its factors what we call atomic weight. * * * The easiest formed element, the one most nearly allied to the protyle in simplicity, is first born. Hydrogen, or shall we say helium,

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[1] *Chem. News*, **54**, 117.

of all the known elements the one of simplest structure and lowest atomic weight, is the first to come into being." Thus, by cooling, the various elements are formed, slow cooling giving distinctly different elements with notable difference in atomic weights, and more rapid cooling giving such analogous groups as iron, cobalt and nickel with slight differences. Crookes made use of the diagram of the periodic system, as devised by Spring and Reynolds, in which the elements lie on an irregular curve described by a constantly lengthening pendulum on which are laid off the atomic weights. The vertical line may represent a sinking temperature, and the oscillations the effect of electricity or chemical energy.

It is scarcely necessary to criticize so fanciful a conception. Little claim to originality can be made for it. Ten years before, Lockyer[1] had announced a "working hypothesis" as to the genesis of the periodic system. This was based upon the examination of stellar spectra. The hotter a star the more simple its spectrum seems to be, the chief lines being those of hydrogen. The cooler ones contain a much larger number of metallic elements and the coolest furnish band spectra characteristic of compounds of elements. This furnishes the framework of his hypothesis.

The hypothesis of Crookes is cited here more for purposes of comparison with the early Greek philosophy. It is an example of the confused, imperfectly wrought out thinking of the present day, which would not have been tolerated by the Greek schools. The two great theories are recklessly mingled. Continuous matter, vaguely called ultra-gaseous, becomes "granulated" or atomic. It is not matter such as we know in the visible universe,

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[1] Nature, **19**, 197.

yet what it is seems a necessary question. It "contains within itself the potentiality of atomic weight" and all forms of energy. Force is not born, matter is not created. There is only a vague something, and yet heat and cooling and electricity and chemical energy are all taking part in the process.

Evolution Theories.

The evolution theories of Wendt,[1] Pryor[2] and others have no foundation in observed facts, and no attempts to adduce facts in support of them have been made. They are in the main modified arrangements of the Periodic System in which the authors see either an undefined and unexplained evolution of the elements from those of lowest atomic weight, or a graded condensation of these lower elements resulting in the formation of those of greater atomic mass. It is unnecessary to describe these speculations in detail.

Are the Elements Composite or Simple?

The arguments in behalf of the composite nature of the elements may well be given here. The reasoning is mainly from analogy, which must often be made use of in science, and yet it is not always safe. When these arguments are duly weighed, however, they cause a wavering in the old faith as to the simplicity of the elemental atoms. Thorpe[3] writes of the "old metaphysical quibble concerning the divisibility or indivisibility of the atom." To Graham the atom meant something which is not divided, not something which cannot be divided. The original indivisible atom may be something far down in the make-up of the molecule.

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[1] "Entwurf zu einer biogenetischen Grundlage für Chemie und Physik," 1891.

[2] *Berlin Phys. Ges.*, **10**, 85.

[3] "Essays in Historical Chemistry."

Remsen says :[1] "The law governing the properties of the elements is known as the periodic law. . . . The so-called elements are shown to be related to one another, and it seems impossible in the light of these facts to believe that they are distinct forms of matter. It seems much more probable that they are in turn composed of subtler elements." Gladstone said[2] in his presidential address before the British association : "The remarkable relations between the atomic weights of the elements and many peculiarties of their grouping force upon us the conviction that they are not separate bodies created without reference to one another, but that they have been originally fashioned or have been built up from one another according to some general plan."

Evidence as to Complexity.

The first argument as to complexity of the atoms is drawn from the manifest kinship shown by the elements in the Periodic System. This has been mentioned and need not be further elaborated. A second argument lies in the analogy of such compounds as ammonia (NH_3), cyanogen (CN), etc., to the elements. Thus the first can easily be classed with the first group in the Periodic System and the second with the seventh group. These resemble elements in every respect except that we can decompose them and build them up at will. The presumption is strong that the same might be done for the elements proper if only the suitable treatment had been discovered.

A further clue to the nature of the elements is afforded in the remarkable change of properties in an element which can be brought about by ordinary means. It is

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[1] *Pop. Sci. Monthly*, **34**, 591.

[2] *Chem. News*, **48**, 151.

almost like the creation of another element. Thus copper is known in a cuprous and cupric condition and the classes of compounds given are as different as if they came from different elements. This is true of a number of other elements. This is not adduced here as a proof of the complexity of the original atoms. It is too obscure for that.

The analogy of the elements to the hydrocarbons has often been pointed out and has its bearing here. These hydrocarbons fall into groups or homologous series with definite increments in molecular weight. A table not unlike the Periodic System can also be fashioned out of them. They can be looked upon as the organic elements out of which all the organic world has been built up, just as the ordinary elements go to form the inorganic side of nature.

CHAPTER VI.

Affinity, The Atomic Binding Force.

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AFFINITY, THE ATOMIC BINDING FORCE.

It was seen from the very earliest times that the hypothesis of the atomic constitution of matter involved also an investigation as to the force which brought about the union of the atoms and held them in combination. This was a problem which the earliest philosophers found themselves incapable of solving because of their general ignorance as to the natural forces and the paucity of their observations and data. And at the present time, summing up all of our knowledge, we can do little more than give this force a name and define some of the laws governing it, which is about the sum of our knowledge in the discussion of all of the forms of energy.

Early Views of Affinity.

The oldest idea as to the cause of the union of two substances was that they must contain some common principle. Thus Hipprocrates (460–357 B. C.) taught as one of the fundamental doctrines that "like would unite only with like."

As has already been seen, at least two ideas were held as to the controlling power bringing about the union One was that of the *νοῦς* or Intelligence—the Directing Spirit. The other was that of *ἀνάγκη* or Necessity—a blind Fate. These ideas appear to have been drawn from the varying beliefs as to the creation of the universe.

The dictum of Hippocrates gave rise to the term at present used, namely affinity, though this ancient belief, cherished for so many centuries after his time, has long.

since been lost sight of. The name affinity is said to have been introduced as follows :[1]

The term *affinitas* seems to have been first used by Albertus Magnus to indicate the cause of the union of sulphur with silver and the other metals. The same expression was made use of by chemists following him and in very nearly the same sense as at present. Glauber, Boyle, Hooke, Barchufen, and others found it useful to designate the unknown combining force. Still, it was inferred that some similarity must exist between the combining substances. The greater the affinity, the greater the chemical resemblance. The term Verwandschaft, or relationship, into which affinity was translated by the German chemists, still further emphasized the same idea.

With the 18th century there came a change in this belief. Boerhaave sought to show that affinity was also evinced by dissimilar bodies in their tendency to combine. Solution was looked upon as an act of affinity, and at first it was held that tin, silver, etc., dissolved in mercury, resins in oils, etc., because they were related, but Boerhaave maintained that the solution of iron in nitric acid was also an act of affinity and that no relationship existed between the two, but that they were essentially different. His influence, as a teacher and the wide distribution of his text-books, secured the introduction and general adoption of his views by chemists. Yet physicists opposed the idea of a new force. Geoffroy tried to avoid this idea by introducing the word *rapport*. Thus two substances united because there existed a *rapport* between them. The term *attraction* used by Newton was adopted by Bergman (as Anziehung), but was too indefinite and general to displace affinity, which by that time had been fully incorpo-

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[1] Kopp : "Gesch.," II, 286, *et seq.*

rated into chemical literature, in spite of the recognition that the latter term was based upon a mistaken idea.

Strength of Affinity.

The knowledge of this force grew very slowly. First it was recognized that the force varied in strength. While many operations in metallurgy and in the experimental work of the earlier chemists indicated this, and for their success were dependent upon it, there were no theoretical observations prior to the time of Glauber. He maintained that the tendency of one body to unite with another differs in accordance with the nature of the latter, and that a substance can bring about the decomposition of such a union when it has a greater affinity for one of the components than they have for one another. Thus he says, that to drive ammonia out of *sal ammoniacum* one must use potash, chalk, or zinc oxide, and not just any earth; sand, clay, etc., are without effect. The action of the potash is due to the fact that it bears a close relation to all acids, is very fond of them and beloved by them, therefore it clings to the *sal acidum* (hydrochloric acid) and the *sal volatile* (ammonia) is set free and distilled off as a subtle spirit.

Thus there were two approximate tests devised for measuring the strength of affinity: the readiness of combination and the displacement of one substance in combination with another. Observations began to accumulate. Glauber and Stahl and others announced certain "affinity series." Thus, for mercury the series of affinity was given as gold, silver, copper and iron. In 1718 Geoffroy published sixteen tables, called by him *tables des rapports;* and then followed a number of tables by different chemists, the best and most widely known being the tables of Bergman in 1775. The following abstract from the table of Bergman will serve to show the principles upon which it was based:

Sulphuric acid.		Potash.	
Wet way.	Dry way.	Wet way.	Dry way.
Baryta	Phlogiston	Sulphuric acid	Phosphoric acid
Potash and soda	Baryta	Nitric acid	Boracic acid
Ammonia	Potash	Hydrochloric acid	Arsenic acid
Alumina	Soda	Phosphoric acid	Sulphuric acid
Zinc oxide	Lime	Arsenic acid	Nitric acid
Iron oxide	Magnesia	Acetic acid	Hydrochloric acid
Lead oxide	Metallic oxides	Boracic acid	Acetic acid
Copper oxide	Ammonia	Sulphuric acid	
Mercury oxide	Alumina	Carbonic acid	
Silver oxide			

In the table the order from top to bottom gives the relative displacing power. Thus in combination with sulphuric acid, where the action takes place in aqueous solutions, baryta is represented as displacing any of the substances placed below it, and so with potash, ammonia, etc. Where the dry substances are subjected to heat the order is changed somewhat.

It was recognized then that the strength of affinity varied with the temperature. This is the *attractio electiva simplex* of Bergman. He recognized also an *attractio electiva duplex*. Macquer made use of the term *affinitas reciproca*, where two bodies seemed to have nearly the same strength of affinity for a third substance, one replacing the other under slightly changed conditions—a partial recognition of the fact that affinity is dependent upon other conditions besides temperature.

This should have sufficed to show the unreliable character of the various tables offered, but chemists were slow to give them up. Nor did they value at its true worth the remarkable work of Berthollet and his conclusion that the action of affinity was proportional to the masses of the interacting substances. This, properly understood, entirely did away with all such tables, for a body with lesser affinity could displace one of greater provided it was present in a sufficiently greater mass.

Definition of Affinity.

To sum up then, chemical force or affinity is the name for that form of energy which brings about chemical union and holds substances in compounds.

1. It appears to act only when these substances are brought within insensible distances of one another, or in actual contact, as it may be roughly expressed.

2. It is an elective force, acting the more strongly the more unlike the substances are, and showing very little energy where they closely resemble one another.

3. The strength of affinity varies readily with the change of certain conditions, especially of temperature.

4. The relative affinity is dependent upon the masses of the interacting substances.

Is Affinity a Distinct Force?

Whether the assumption of a new force is necessary, or whether the phenomena of chemical change can be referred to one of the other physical forces, has long been a disputed question. Berzelius, Le Sage, Berthollet and others have endeavored to do away with the necessity for the assumption of a new force. The question cannot yet be decided and until the problem is solved the assumption of a new force is necessary.

It is well to give some of the views which have been expressed In Berthollet's "Essai de statique chimique," which, as Lothar Meyer says, " stands in the midst of our immensely extended literature like a lost landmark, to many perhaps unknown, studied by the few, completed and perfected by none," the author supposes that what is known as affinity is probably "a phase of the same fundamental property of matter as that to which universal gravitation owes its origin." It is evident that these two phases of force exhibit important differences. These he attributed to the proximity of the reacting substances in the case of affinity and to the influence of special conditions. The complexity of chemical phenomena and our ignorance of them prevented, he thought, the application of the principles of mechanics to them. To acknowledge this would remove chemistry still farther from the position of an exact science. To quote again from Lothar Meyer:[1] "If chemical phenomena are not to be regarded as resulting from the actions of chance, then it must be acknowledged that they are subservient to the general principles of mechanics, to the laws of equilibrium and of motion, and that 'the curve described by a single atom is as fixed as the path of a planet, and between the two cases no other difference exists save that resulting from our ignorance.'[2]"

Le Sage[3] would explain chemical phenomena by the movement of the ultimate particles, a conception which has been made use of by physicists to explain all attraction of matter. The efforts of Le Sage could not be other than crude at that stage of the science; still the kinetic theory has served to explain many of the phenomena of molecular physics, and there is much promise in this direction. The development of chemical statics and dynamics should be the final aim of chemical research, if the motion of matter and the equilibrium of force is to be understood.

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[1] "Modern Theories of Chemistry," Introduction (Eng. Trans., London, 1888).

[2] Laplace: "Essai phil. sur les probabilities," 3me Ed., Paris, 1816, p. 6.

[3] Le Sage: "Essai de chim. mech.," 1758.

Explanation Offered by Berzelius.

Berzelius offered as an explanation of affinity the hypothesis that it was dependent upon electrical attraction. The rôle played by electrical attraction in chemical phenomena is certainly a most important one, but it is easy to push this idea beyond the point justified by known facts. This was done by Berzelius in his electrochemical theory. This theory seems to have been first a conception of Davy, a kind of philosophical vision of the two forces, electrical and chemical, existing side by side everywhere in nature and holding all things in equilibrium. It is not strange that such an idea should have arisen in the mind of one who had already worked such wonders by means of this force, electricity, whose study and triumphs were just beginning. It was Berzelius, however, who really enunciated the theory, basing it upon experimental investigation and making it the basis of a system of chemical classification which, modified according to increasing knowledge, is still the best that chemists have to offer.

Berzelius emphasized the fact already noted that chemical affinity was most strongly exhibited between atoms which were most unlike. The wide difference in intensity of action between different atoms was also considered, some showing almost no affinity for one another, and others very great. The explanation offered was that this exhibition of affinity depended upon the electrical states of the atoms. The basis, in fact, for these views was twofold. First, compounds are decomposed by the electric current, and when thus decomposed their constituents invariably seek the same respective poles. Again, chemical union can be caused by the action of electricity, and chemical action is commonly accompanied by electricity.

According to the ideas of Berzelius, each atom is endowed with a certain quantity of electricity, partly positive and partly negative, which accumulates in particular parts of the atoms, giving to each a positive and a negative pole. The atom as a whole, however, has the character of either a positively or a negatively electrified body because of the preponderance of one or the other kinds of electricity. When two atoms combine, their respective charges of electricity are neutralized. Of course this offers an explanation of the greater attraction between unlike atoms, as bodies similarly electrified exert little or no attraction upon one another, while with dissimilar charges the reverse is true. Every molecule, then, was built up of two parts, one positively and the other negatively electrified, and thus formed a dual structure. The theory was known as the Dualistic Theory. The theory practically identifies chemical affinity with electrical polarity.

Measurement of Affinity.

It is evident that an accurate measurement of the relative attraction between different atoms is necessary as a preliminary to the study of the force. The difference between the attraction exerted between a hydrogen and a chlorine atom and that exerted between hydrogen and oxygen, or any other atom, must be known, and it must be known also whether this action is dependent upon the nature of the atom or only upon the interacting masses.

It is a matter of ordinary observation that such differences exist. Certain elements combine easily and form stable compounds, others combine with difficulty and form unstable compounds. A certain rough gradation can be observed also in the affinity between an element and the members of a group or family. Thus rough measurements can be formed by careful observation of chemical reactions, but they leave much to be desired in the way of definiteness and accuracy.

Disturbing Influences.

In seeking to measure affinity by such observation of chemical reactions it must be borne in mind that there are disturbing influences. Such an influence can readily change the order in which the breaking-up of a union of atoms takes place so that it shall not be determined by the relative affinities. One of the most common disturbing influences is the change of physical state. For instance, in a reaction between two substances, A and B, a third substance, C, may be formed which is a gas at the temperature of the reaction. As each particle of C is formed it escapes from the reaction or, as is said, from the sphere of action. It is manifest that a new equilibrium will be striven for, the formation of C will continue, resulting in a final equilibrium of products possibly quite different from the result had C remained in the sphere of action.

A concrete example is that of sulphuric acid acting upon a chloride. At a slightly elevated temperature, gaseous hydrochloric acid is formed and this will continue until the sulphuric acid has replaced all of the hydrochloric, and the old inference was that the affinity of the sulphuric acid for the base was stronger than that of hydrochloric acid. When we compare these acids by other methods, however, in which they are held under the same conditions, the hydrochloric acid is seen to have the stronger affinity.

The chief disturbing conditions, then, are those under which certain of the resulting products are removed from the sphere of action ; it may be as gas or as a solid precipitated from solution. An instance of the latter class may be seen when sodium chloride is added to lead acetate. As is well-known, lead chloride will be precipitated, and yet the affinity of chlorine for lead is less than for sodium. As to why the reaction should begin at all and even a single particle of lead chloride formed introduces another phase of the study of affinity.

It is manifest then, that merely observation of chemical reactions will lead to most erroneous ideas as to the relative strength of affinities, besides failing to lead to a definite, direct comparison with any standard.

Heat of Chemical Reactions.

Chemical action is attended by the evolution or absorption of heat. Let us consider the union of hydrogen and chlorine. It is evident that a measure of the affinity between the atoms of these elements could be arrived at if the heat produced by their combination could be determined, and if it could be directly referred to the transformation of potential energy of isolated atoms at rest into kinetic energy, the molecules produced being at rest. But it is not in accord with our best knowledge to suppose the atoms to be originally isolated nor at rest, and hence unknown factors are introduced into the equation and the problem is a complex one. Of course, the effort at measuring chemical affinity through the heat produced is dependent upon Mayer's Law of the Conservation of Energy, that in the transformation of physical forces the production of one is accompanied by a proportional expenditure of the other. The measurement of the heat evolved in chemical reactions has led to the development of the branch of chemistry known as Thermochemistry.

The first law deduced was that of Lavoisier[1] and Laplace namely, that for the decomposition of a compound into its constituents the same amount of heat is absorbed as was evolved in its formation.

In 1840 Hess[2] announced the important principle that in a chemical reaction the amount of heat evolved is the same whether the process takes place in one step or in separate steps. This removed many difficulties which lay in the way of the determination of this evolved heat. Thermochemistry was further built up by the work of Favre and Silbermann, and especially by that of Thomson.

Deductions from Thermochemistry.

How far do the large number of observations gather help in the measurement and study of affinity? To examine this question let us take again the formation of hydrochloric acid by the union of hydrogen and chlorine. If the present views are correct, the first thing that takes place is a decomposition of the molecules of hydrogen and chlorine. This means an absorption of heat, and hence the heat observed in the reaction is less by that amount than the total amount evolved. The heat measured is really the difference between two quantities whose absolute values are unknown. This is true of every chemical reaction, and the heat evolved or absorbed in any one reaction cannot be taken as a measure of affinity.

It is possible, however, to arrive at some knowledge of relative affinities by the study of analogous reactions. Thus, in the union of hydrogen with chlorine, bromine, and iodine the heats of formation are respectively 44.000, 16.880 and 12.072 calories. These are not to be taken as

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[1] "Oeuv. de Lav.," **11**, 287.

[2] Pogg. *Ann.*, **50**, 385.

proportional to the affinities of chlorine, bromine and iodine for hydrogen, but simply as varying in the same order. As Remsen says: "The difficulties are much increased in more complicated cases and it will, therefore, be seen that it is impossible to measure the affinity by means of the heat evolved in reactions."[1]

Molecular Affinity.

It is manifest from what has been said that affinity in the strictest sense, that is, the direct attraction between single isolated atoms, is never dealt with alone in chemical reactions and, therefore, does not come within the field of investigation. The attraction considered is that of atoms in molecules and is much more complex. It is a resultant of the affinities of the atoms composing the molecules. This is the only possible deduction from the molecular theory of the day. All measurements then must represent these resultants. An instance of the use made of these measurements is seen in the question of the neutralization of acids and bases.

Heat of Neutralization.

A study of the heats of neutralization of acids and bases has rendered it possible to correct such tables as those given by Bergmann and others at the close of the 18th century, giving a truer picture of the affinities of the acids. Equivalent quantities of different acids are neutralized by the same base and equivalent quantities of different bases are neutralized by the same acid, and the heats of the reactions are carefully measured. The reactions are studied in aqueous solutions. The strengths of the acids thus measured are called by Thomsen, who has done most of this work, the acid avidities. What this strength of avidity really is, of course, cannot be stated. It is only known as a somewhat vague property.

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[1] Remsen: "Theoretical Chemistry," p. 290.

AVIDITIES OF THE ACIDS.[1]

1	molecule	nitric acid	1.00
1	"	hydrochloric acid	1.00
1	"	hydrobromic "	0.89
1	"	hydriodic "	0.79
1	"	sulphuric "	0.49
1	"	selenic "	0.45
1	"	trichloracetic "	0.36
1	"	orthophosphoric acid	0.25
1	"	oxalic "	0.24
1	"	monochloracetic "	0.09
1	"	hydrofluoric "	0.05
1	"	tartaric "	0.05
1	"	citric "	0.05
1	"	acetic "	0.03
1	"	boric "	0.01
1	"	silicic "	0.00
1	"	hydrocyanic "	0.00

If the heat evolved in the reaction between acids and bases is known, an idea can be formed as to what takes place when an acid acts upon a salt. As in most of these cases no action is evident, it is plain that light can be thrown upon it only by some such means as the measurement of the heat of reaction. It has been shown that some action always takes place, and that the base is divided between the two acids, however weak the free acid may ordinarily be regarded. Generally, more will go to one acid than to the other. The division between the acids can be measured, and, since equivalents are used, an idea of the relative strength is obtained. This measurement is used in connection with the table just given. Probably the most important lesson to be deduced from this work is that in a solution, containing a base and two or more acids, the base is always divided between the acids and does not all go to the one with the strongest affinity.

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[1] Thomsen : "Thermochemische Untersuchungen," 1882, **1**, 308.

Mass Action. The observation that a base is divided between the acids in a solution and not all combined with any one, leads to the influence of mass in chemical reactions. The Law of Mass Action, however, was first given by Berthollet many years before these observations were made. According to his view, affinity was essentially the same as gravitation. The deduction drawn by him from his experiments was that "every substance which tends to enter into combination acts in proportion to its affinity and its mass." This remarkable generalization was given to the world at a time when the study of the atom was just beginning and when all were busied with the establishment of the new laws of constant and multiple proportions, the determination of atomic weights and the amassing of other facts necessary for the foundation of the new chemistry. It was the culmination of the old chemistry, and with the passing away of that and the defeat of Berthollet's contention against the law of constant proportions, it fell into undeserved oblivion. It was many years before it was taken up again and bore fruit in the science. The criticism of Gmelin in 1852 will exemplify the estimate generally placed upon Berthollet's work by chemists during the first half of the 19th century.

" There remains for Berthollet the great service of having tested with sharp insight the doctrine of affinity and of having observed it from a new point of view, directing attention to the influence of cohesion and elasticity upon the exhibited effects of affinity. But he laid too little weight upon the strength of affinity and much too great upon the amounts of the substances entering into reaction and upon the influence of cohesion and elasticity. He wrongly assumed that a substance which separated as a solid was out of the sphere of chemical action ; that substances could combine with one another in all possible proportions, and that a substance divided itself between two others in the proportion of their chemical masses."

Support for Berthollet's Views.

The first support of Berthollet's views upon analytical data came through the observations of H. Rose[1] in 1851. Rose pointed out that while carbon dioxide and water are reputed to have but weak affinities, yet acting on a large scale through the centuries they have decomposed most stable and resisting compounds which go to form the earth's crust. A number of laboratory experiments showed the decomposition of various salts by water. In the case of certain carbonates and borates, it was proved that, with the increasing amount of water, the acid was withdrawn from the salt in increasing amount.

Margueritte and Tissier undertook to confirm the deductions of Berthollet in the following manner. On dissolving sodium chloride in a solution of potassium chlorate more will be taken into solution than corresponds to the solubility of sodium chloride in pure water. From this they concluded that the more soluble potassium chloride and sodium chlorate were formed in the solution. Also, if sodium chloride is added to a saturated solution of potassium chlorate, more of the latter will go into solution. Again, if barium, strontium or calcium carbonate is added to a solution of ammonium chloride which reacts weakly acid, the reaction becomes strongly alkaline, showing the formation of ammonium carbonate, and the barium, etc., are found in the solution as chloride.

Many similar observations were added. Thus, copper sulphate is not reduced by glucose, while copper acetate

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[1] Pogg. *Ann.*, **82**, 545.

is. If glucose is added to a hot solution of copper sulphate there is no reduction, but if sodium or any other acetate is added copper acetate is formed and immediate reduction takes place.

Again, we have the decomposition of insoluble salts by soluble. Barium sulphate can be changed into barium carbonate by boiling with a solution of potassium carbonate. The action is limited, however, and ceases long before all the potassium carbonate has been transformed into potassium sulphate. The reaction can be reversed, and barium carbonate can be rapidly changed to barium sulphate by boiling with a solution of potassium or sodium sulphate. In the case of calcium and strontium the sulphates are more easily changed to carbonate than in barium sulphate, but the reverse reaction does not take place.

Rose was not clear in his explanation of these phenomena, though he ascribed the complete decomposition of calcium and strontium sulphate to their greater solubility and the partial decomposition of barium sulphate to the action of the soluble sulphate formed upon the insoluble carbonate formed at the same time, thus forming again insoluble sulphate.

Malaguti[1] gave the following explanation: When barium sulphate is acted upon by potassium carbonate, at first only barium carbonate and potassium sulphate are formed. As soon as these are formed, however, the opposite reaction sets in, though slowly and with little energy at first, as but small amounts are present. As the first reaction goes, it becomes slower from the decrease in the quantities of the reacting bodies, while the opposed reaction increased for the opposite reason. When these two reactions are equal in speed the whole is in equilibrium and apparently stationary.

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[1] *Ann. chim. pharm.*, (3), **51**, 328.

A great many such reactions were investigated by Malaguti, and certain generalizations were deduced by him, but as they have very little direct bearing upon the influence of mass they will not be referred to further in this work.

The knowledge of the conditions existing in homogeneous solutions was further advanced by the investigations of Gladstone. The investigation of such solutions presents many difficulties and uncertainties. Malaguti[1] had used two salts with different acids and bases, both of which were soluble in water but only one soluble in alcohol. The solutions were mixed and then an excess of alcohol added. The precipitate formed was then analyzed—a method open to serious objections. Gladstone[2] used a colorimetric method. For instance, various ferric salts are mixed with sulphocyanides. The blood-red ferric sulphocyanide is formed. He found that all of the iron was never changed and the amount of change depended upon the nature of the acid combined with the iron and the base combined with the sulphocyanic acid. The further addition of either ferric salt or sulphocyanide to a mixture of equal amounts of the two increased the amount of red salt continuously and not step-wise, as would be the case if the interchange depended upon the formation of new compounds, as had been maintained by Bunsen and Debus in other cases. Gladstone concluded:

1. That if two or more binary compounds were mixed so that all existing compounds are free to act upon one another, each positive element enters into combination with every negative element and in constant, definite proportions.

2. These proportions are independent of the manner in

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[1] *Ann. chim. pharm.*, (3), **37**, 198.

[2] *Phil. Mag.*, (4), **9**, 535.

which the various elements were originally combined. They are, further, not merely the resultants of the different affinities between these elements but also depend upon the mass of each substance present.

3. A change in the mass of one of the compounds brings about a change in each of the others, and this change progresses continuously. A sudden step-like change is possible only when one substance combines with another in more than one proportion.

4. The equilibrium arranges itself generally in a very short time, but often the final condition is reached only after the lapse of hours.

5. The phenomena are quite different when precipitation, volatilization, crystallization or similar changes take place, the equilibrium continually changing with the removal of any of the compounds.

Diffusion and circular polarization have been suggested as additional methods for the examination of homogeneous solutions. In 1862 considerable progress was made by the investigations of Berthelot and St. Gilles upon the formation of ethers by the action of acids upon alcohols. These reactions were especially adpated to this study because they took place slowly and because a simple titration revealed the progress of the reaction. Here we reobserved typical cases of reciprocal or reversible reactions in which the products formed by the change in the original compounds call forth an opposed reaction reforming the original compounds. Thus alcohol and acid form ether and water, and from the mixture of ether and water acid and alcohol are once more formed. The tendency is to a final state of equilibrium. This limit is nearly independent of the temperature. It is dependent upon the relative masses of the reacting substances.

Influence of Heat upon Affinity. The union of the elements in most compounds is overcome by a rise of temperature. Some can remain in combination only at very low temperatures, others are decomposed only by very high temperatures. The opinion is generally held that at sufficiently high temperatures no union can take place nor compounds exist. At such temperatures chemical elements, if they exist as such at all, must be in the atomic condition. It also seems to be true that at sufficiently low temperatures there is little exhibition of affinity. Thus the strongest mineral acids fail to react with the strongest alkaline hydroxides when the temperature approaches 100° above absolute zero.

Kinetic Theory. The facts above noted confirm in the strongest manner the application of the kinetic theory by Williamson.[1] He was led to the assumption that in an aggregation of molecules of each compound a continuous interchange goes on. Thus, in a vessel filled with hydrogen chloride each atom of hydrogen does not remain quietly in connection with an atom of chlorine, with which it first entered into combination, but there is a constant interchange of place with other atoms. Suppose we mix hydrochloric acid and copper sulphate, then the hydrogen atom does not merely interchange with other hydrogen atoms, but may replace a copper atom. So, too, any mixture of salts will reveal, when examined at any time, the bases distributed among the different acids. A few years later Clausius[2] made use of the same supposition to explain the phenomena of electrolysis. In gases and liquids he assumed the molecules to be in active motion, and that more or less frequently phases arose in which the molecules were partly

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[1] *Ann Chem.* (Liebig), **77**, 37.

[2] Pogg. *Ann.*, **101**, 338.

separated and could exchange their components. He did not consider, as Williamson did, that this exchange affected all molecules, but it was sufficient if only an occasional molecule was so decomposed. With rise of temperature there is a more frequent separation of molecules and a more rapid interchange of components. An important feature of the hypothesis of Clausius is the difference of condition supposed to exist between the molecules at any fixed temperature.

This hypothesis offers a plausible explanation of dissociation phenomena as well as those of electrolysis. Dissociations are not sudden when such and such a temperature is reached, but are more or less gradual phenomena. The hypothesis also throws light upon the state of equilibrium in chemical reactions, upon reversible reactions, and upon the influence of mass action. Equilibrium in chemical reactions must be looked upon not as static but dynamic. It is no stationary equilibrium of forces but one of opposing processes. Since this equilibrium is dependent upon the number of molecules which bring about the direct action and of those causing the reverse action, it must be dependent upon the relative masses of the different substances. All reactions may be looked upon as reciprocal. Only, if in any way one or the other of the products formed is removed from the sphere of action the reverse reaction cannot take place.

Theory of Ions.

From an entirely different line of reasoning, Arrhenius arrived at a similar theory of solutions to that proposed by Williamson and Clausius. In the case of water solutions of salts, strong acids, and bases, the relations observed between such constants as the boiling-points, freezing-points, etc., and the molecular weights do not hold good. The calculations would show a larger number of molecules than the formulas indicate. It should be stated that the divergence is greater in more dilute solutions. In concentrated ones it is often scarcely observable. In very dilute solutions of some salts there are apparently 2 molecules present for every one added. Arrhenius suggests that in these cases the dissolved substances are, by the action of the water, separated partly or entirely into their ions. Thus in sodium chloride there would be sodium ions and chlorine ions. Its name comes from the Greek *ἴημι* (I go) and is taken from the terminology of the electrolytic theory with its kathodes and kathions, anodes and anions. The theory supposes the ions to be highly charged with electricity. Their constant motion brings them into contact with one another, and thus combinations are being constantly formed and broken up. Under the action of an electric current the ions positively charged seek the negative pole, while those negatively charged seek the positive pole.

There are many difficulties in the way of the acceptance of this theory and in some respects it is not a satisfactory solution of the problems. It is still under discussion. Manifestly it is of very limited application, whatever of truth there may be in it, since it applies fully only to certain bodies dissolved in particular solvents and then only in very dilute solutions.

Guldberg and Waage.

The first efforts at a mathematical formulation of the relation between the mass and the corresponding chemical action were those of Guldberg and Waage.[1] The fundamental principle is that the action is proportional to the mass entering into the reaction. This is virtually a re-

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[1] "Études sur les affinites chimiques," 1867; *J. prakt. Chem.*, (2), **19**, 69.

statement of Berthollet's views. The action of two bodies upon one another is then proportional to the mass of each, this mass being the amount contained in a space unit. If the amount of one is zero the action is zero. The intensity of the interaction must be measured by the product of the active masses. The action is further dependent upon the nature of the bodies, the temperature and other circumstances. These influences were considered together under the name of coefficient. If p and q represent the active masses and k this coefficient, then

$$\text{chemical force} = kpq.$$

In the case of reversible reactions the equilibrium is

$$kpq = k'p'q',$$

where k', p' and q' represent the factors of the opposite reaction. If equivalent masses of the original substances were taken (P, Q and P′, Q′), they do not remain in chemical equilibrium but an amount x is transformed from P and Q into P′ and Q′. Thus P becomes $P-x$; Q is changed to $Q-x$; P′ to $P'+x$; Q′ into $Q'+x$. If v is the total volume, then for the active masses in condition of equilibrium we have

$$p = \frac{P-x}{v}, q = \frac{Q-x}{v}, p' = \frac{P'+x}{v} q' = \frac{Q'+x}{v}.$$

Inserting these values in the equation for equilibrium, the following equation is gotten:

$$(P-x)(Q-x) = \frac{k'}{k}(P'+x)(Q'+x).$$

If x is determined from any special case, then $\frac{k'}{k}$ can be calculated and thus can be predicted for any chosen original masses the size of x and the distribution of the compounds upon the setting in of equilibrium.

The important advance over Berthollet in this work is the demonstration that the state of equilibrium is not determined by the original masses but by the masses present at the moment of equilibrium. It has been shown that the results obtained through the study of the heats of neutralization accord with the theory of Guldberg and Waage, and what Thomsen called the avidity of acids and bases is the same as the coefficient of affinity in the equation of Guldberg and Waage.

Velocity of Chemical Change. The same authors expressed also in a formula the relation between the velocity of reaction and the chemical equilibrium. They gave the reaction velocity as proportional to the active force

$$v = \mathrm{OT}$$

where $v = \frac{dx}{d\mathrm{I}}$, the ratio of the transformed mass dx to the time $d\mathrm{I}$; T is the force $= kpq$, and O is a factor.

For the reciprocal reaction

$$v = \mathrm{O}(\mathrm{T} - \mathrm{T}') = \mathrm{O}(kpq - k'p'q').$$

When equilibrium is reached $v = \mathrm{O}$ and the original equation is restored.

$$kqp = k'p'q'.$$

These equations accord well with experimental results.

Other Methods. The law of mass action has been tested further by Ostwald by the changes brought about in volumes. This is done by observations on the specific gravities of solutions. The thermochemical method is difficult and requires large amounts of substance. The volume-chemical method is comparatively easy and 1/50 the amount can be used. He also made use of a third method, the measurement of the coefficient of refraction, which could be carried out with still smaller amounts. The investigation can be extended to bodies insoluble in water, the solubility of such in dilute acids giving a measure of the coefficients of affinity. Results obtained by these methods coincide with those already given.

The simplest method of all is the electrical method. This consists in determining the conducting power of solutions of various dilutions. This is the method which has been most largely made use of.

Conclusions. It is clear that in these measurements of the so-called coefficients of affinity we are dealing with something quite vague and unknown, and the bearing upon what has been called affinity or chemical force is far from clear. Still some progress has been made in our knowledge of this force. The first law of the mechanical theory of heat referring to the relation between the forces is obeyed, and this is the foundation of thermochemistry. Again it would seem that there is some connection between this attraction and the electrical states of the atoms. Much stress has been laid upon this, but little is really understood concerning it. Thus, until it is explained why two bodies at rest, similarly charged with electricity, repel one another while two parallel wires with currents of electricity of the same order attract one another, we can know little of the effect of electric charges in atoms in constant motion in all directions and at a high speed.

Again, if the kinetic theory is true, the attraction is of such a character as to admit of freedom of motion among the atoms, along with a continuous interchange of atoms, one replacing the other. How this is possible in complex systems without a breaking-down of the system is not clear, nor yet why the interchange should be restricted to certain atoms only and not hold good for any or all.

Lastly, the attraction, while elective, is exhibited between all atoms coming into the sphere of action. Thus when the compounds AB and CD are brought into the same sphere of action, even though the affinity of A for B is many times greater than A for D, the attraction is such that some of the A atoms give up B atoms and unite with D, and the larger the number of D atoms, or of molecules of the compound CD, the larger the number of AD molecules formed, until most of the original AB molecules can be broken up. The number of D atoms combined with A may be less than 0.01 part of the total number present. This is the influence of mass and has a most important bearing upon the nature of chemical force. It is evident that we are very far from a satisfactory understanding of the whole matter.

Molecular Attraction.

In what has preceded, the attraction between atom and atom has been chiefly considered. It is not possible to say how closely this is related to the kind of attraction which exists between molecule and molecule, nor the relation of either to gravitation. There is a field here for much work. It is of interest to cite here a recent examination of some of the laws governing molecular attraction. The modern theory of solutions has made it very probable that the total kinetic energy of a gaseous and a liquid molecule at the same temperature are the same. The internal laten heat of vaporization may, therefore, be taken as a measure of the work done in increasing the distance apart of the molecules. A study of this relation by Mills[1] seems to give some ground for the belief that the molecular attraction varies inversely as the square of the distance between the molecules, and does not vary with the temper-

[1] Molecular Attraction : *J. Phys. Chem.*, 1902, p. 209.

ature, to this extent resembling the attraction of gravitation.

CHAPTER VII.

Valence.

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VALENCE.

Very closely connected with the phenomena of affinity are those of valence. Here again the question arises as to whether the assumption of a new force is necessary. Affinity is sometimes called the qualitative combining force, and valence the quantitative combining force. If there is no affinity between two atoms, then no valence can be exhibited. Should an atom have no affinity at all for any of the other atoms, then it has no saturation capacity or valence. The question of valence did not arise in chemistry until there had been some development of the theories as to affinity. No necessity was felt for it until the number of known compounds had been greatly multiplied and the need for their classification became pressing.

Definition of Valence. Valence may be defined as that property of the atom which decides the number of atoms of some other element with which it may combine. It does not refer to the ease or difficulty of combination, nor to the stability of the compound formed, but simply to the number of atoms combined with the atom under question.

If the theory of atoms is accepted and the validity of the methods in use for determining the number of atoms in the molecule be granted, then the following facts are arrived at. There are series of compounds whose composition is represented by the following formulas :

ClH	OH_2	NH_3	CH_4
BrH	SH_2	PH_3	SiH_4
IH	SeH_2	AsH_3	

Li_2O	BeO	B_2O_3	CO_2	N_2O_5	SO_3	Mn_2O_7	OsO_4
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SeO_3		RuO_4
K_2O	CaO	Fe_2O_3	PbO_2	As_2O_5	TeO_3		

A glance at these classes of compounds shows that certain elements combine with hydrogen in the ratios of 1 atom with 1; 1 to 2; 1 to 3; and 1 to 4. And so in the case of the oxygen compounds there is a varying number of atoms of oxygen taken into combination depending upon the nature of the element. The number of atoms of a standard element with which a single atom of an element will combine, has been called the *chemical value* of that element. The power of combining with a certain number of atoms of the standard is known as the *combining capacity*, *capacity of saturation*, *quantitative combining power*, or the *valence* of the atom. This has also been defined as the ratio between the equivalent and the atomic weight of an element. The term *equivalent*, it will be remembered, signified the number obtained by analysis without the introduction of any theoretical considerations. It was simply the combining number. Thus, with hydrogen as the standard, and equal to 1, the equivalent of chlorine is 35.4; of bromine, 80; of iodine, 127; and these numbers are also the atomic weights of these elements. Therefore, the ratio is 1 and the valence 1. Again, the equivalent of oxygen is 8; of sulphur 16. The atomic weights are 16 and 32 respectively. Hence the valence of oxygen $= \frac{16}{8} = 2$; of sulphur $= \frac{32}{16} = 2$.

It is quite clear from what has been said that so long as the methods for determining atomic and molecular weights were in question, and indeed the atomic theory itself on trial with equivalents freely substituted for atomic weights, that no need for the idea of valence would be felt. Indeed no clear conception of this property could arise. With a fuller knowledge of the molecule it became evident that an extension of the atomic theory was called for. In considering the union of atoms in a molecule, two distinct conceptions are necessary. First, that of a power bringing about the union of the atoms, and, secondly, something which places a definite limit to the number of atoms which can enter into the union.

Evolution of the Idea.

Probably the first conception of valence was in the recognition of the so-called polyatomic compounds. This term was first used by Berzelius[1] in 1827, he applying it to such elements as chlorine or fluorine where he thought several atoms of these elements united with a single atom of another element. This use of the term does not seem to have received wide acceptance. It was applied, however, to compounds, and for certain of these its use became general. Thus Graham applied it to the acids combining with various proportions of the bases. These were called polybasic acids. Odling and Williamson extended the idea to the compounds which, according to the theory prevailing at that time, were built upon types. Thus both the type theory of Laurent and the substitution theory of Dumas were involved in the evolution of this conception. The substitution of elements for one another would naturally lead up to the idea of the relative value of their atoms. This was called by Liebig the *replacement* value.

Polybasic Acids.

As we are dealing here with the growth of a theory, it is important to examine the steps in detail. The earlier idea held by Gay-Lussac, Gmelin and others as to the formation of

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[1] "*Jahr. d. Chem.*," 7, 89.

neutral salts was that in the metallic oxides 1 atom of metal was united with 1 atom of oxygen and these metallic oxides united with 1 atom of acid. Graham's work upon the acids of phosphorus showed that in the ortho acids for 1 equivalent of phosphorus pentoxide there were 3 equivalents of what he called "basic water" which could be substituted by equivalent amounts of metallic oxides. In the case of other acids, he maintained that this basic water was present and the number of equivalents of it determined the number of equivalents of metallic oxides which could enter into combination with it. Therefore, he reasoned, the saturation capacity of these acids was dependent upon the basic water belonging to their constitutions. Liebig extended this to many other acids and distinguished between mono-, di-, and tribasic acids, and the property was spoken of as the basicity of the atoms.

The Work of Frankland.

The idea of basicity was farther extended to the compound organic radicals and played a part in the theories of type, pairing, etc., which obtained in organic chemistry. In his studies upon the organo-metallic bodies Frankland noticed that arsenic when united with methyl changed its saturation capacity. Arsenic was capable of uniting with 5 atoms of oxygen. The highest oxide of cacodyl, the arsenic-methyl compound, had only 3 atoms of oxygen. Similar observations on other organo-metallic bodies led him to the following conclusion:[1] "When one observes the formulas of inorganic compounds, even a superficial observer is struck by their general symmetry. . . . Without making an hypothesis as to the cause of this agreement in the grouping of the atoms, it is clear

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[1] *Ann. Chem.* (Liebig), **85**, 368.

that such a tendency exists and that the affinity of the atom of these elements is always satisfied by the same number of atoms without any reference to the chemical character of these atoms.'' All of Frankland's conclusions would not now be accepted, but he deserves the credit of first gathering the facts bearing upon it and announcing this new property of the atom. The idea of saturation capacity was thus extended from the radicals to the elements.

A Relative Property.

It will be readily seen that whether hydrogen unites with 1 or 2 chlorine atoms is as much determined by the chlorine as the hydrogen atom. So, too, the fact that 1 oxygen atom unites with 2 hydrogen atoms is decided by both the oxygen and the hydrogen atoms. It can not be spoken of as an inherent property of the hydrogen atom, nor of the chlorine, nor of the oxygen, but is rather a relative property evinced only when the different atoms come within the influence of one another and is the resultant of that mutual influence. All attraction is, of course, mutual and relative. It is necessary that some one element shall serve as a standard. It will be seen that there are difficulties in the way of this. Still, hydrogen is ordinarily assumed as the standard. An atom which combines with 1 atom of hydrogen or its equivalent, is univalent; with 2 atoms is bivalent; with 3 is trivalent; with 4 is quadrivalent, etc. Of course where the element combines directly with hydrogen, as chlorine, sulphur and nitrogen, there is no difficulty in deciding upon its valence. Where it does not combine with hydrogen it may be compared with some other element which does so combine, but here serious difficulties arise. If valence does not mean the absolute value of an atom but is the result of the mutual influence of different atoms and dependent upon their nature, is it right to assume that the valence toward some other atom can be directly compared with the standard? Even a slight examination of the compounds will show that such a conclusion is not justified. The valence of a number of elements compared with hydrogen differs widely from that gotten by comparison with chlorine or oxygen. Thus phosphorus forms the compound PH_3. Its valence with hydrogen as a standard would be 3. With chlorine it forms two compounds, PCl_3 and PCl_5. Here its valence is either 3 or 5. With oxygen it gives the compounds, P_2O_3 and P_2O_5. The composition of water is H_2O, and so oxygen would appear to be bivalent. Any element which combines with oxygen in the ratio of 2 atoms with 1 may be considered to have the same valence as hydrogen. If the compound with oxygen is in the ratio of 1 atom with 1, the element is bivalent, as oxygen is. If 2 atoms of oxygen to 1 of the element, then it is quadrivalent. But most of the elements form several oxides. Thus gold gives Au_2O and Au_2O_3 and we are left in doubt as to whether it is univalent or trivalent. Manganese has the following oxides: MnO, Mn_2O_3, Mn_3O_4, MnO_2 and Mn_2O_7, giving thus wide range of choice. Taking extremes, we may apparently have sulphur bivalent toward hydrogen, quadrivalent toward chlorine and sexivalent toward oxygen; iodine univalent toward hydrogen, trivalent toward chlorine, quinquivalent toward fluorine and septivalent toward oxygen.

Valence Variable. The variability of valence has been a disputed point among chemists. It would seem from the standpoint of present knowledge that there is little ground for doubting the variation both towards different elements and towards one and the same element. Remsen[1] says: "Valence is plainly variable, if we consider the composition of the compounds which an element forms as final evidence of the valence of that element. If we consider valence as due to something residing in atoms, it is difficult to conceive of this something as being variable, any more than we can conceive of the weight of atoms as variable. How can one and the same atom have at one time the power to combine with one univalent atom and at another time three or five times that power? If it has the power to combine with five univalent atoms once, it seems most natural to suppose that it would always have that power." The opposite view of the invariability of valence was generally held at first and has been maintained very stubbornly.

In developing the constitutional formulas for organic substances, Kekulé[2] assumed the valence of the elements to be a constant magnitude. He maintained that atomicity was a fundamental characteristic of the atom, which was just as constant and unchangeable as the atomic weight itself.

One of the first applications of the doctrine of valence was to the carbon atom. Kekulé assumed for this a valence of 4, and the constitution of all organic compounds was explained on this hypothesis, the dominant theories in that field still having this for a basis. In later years even this stronghold for constant valence has received some sharp attacks. It is not strange that a constant valence should have been assigned to the other atoms and vigorous means used to force the formulas for their compounds into agreement with it.

[1] "Theoretical Chemistry," p. 91.

[2] *Compt. rend.*, **58**, 510.

Molecular Combination. Where the formulas did not admit of forcing and the variation in valence remained, various special hypotheses were devised to account for it. Thus it was supposed that there were two classes of compounds—atomic and molecular. The former were true chemical compounds, and in them the atoms exhibited all of their usual properties, including valence. In the second class a new force was called into play, acting between the molecules and binding them together. Through affinity the molecules are first formed, and in them valence has its part to play. Then these molecules attract and bind one another together, and in this atomic valence has no part. Thus we have salts with their water of crystallization in which molecules of the salt are supposed to bind molecules of water. Further, we have such compounds as PCl_5 and NH_4Cl. This distinction was chiefly based upon the comparative ease of dissociation of the so-called molecular compounds by means of heat. The water of crystallization is more easily dissociated from the salt than either salt or water can be. Phosphorus pentachloride readily decomposes into the trichloride and a molecule of chlorine, and ammonium chloride becomes ammonia and hydrochloric acid.

Objections to the Hypothesis. If the investigation is restricted to a few such compounds as these it might be granted that enough difference is shown in stability to give some foundation for the hypothesis, but there are a number of other cases in which the assumption will not hold. Thus while the explanation might suffice for PCl_5 it will not cover the case of $POCl_3$ which can be volatilized without decomposition and has every claim to be considered a true chemical compound. Again, all the ammonium salts would have to be explained as molecular compounds. The analogy of these bodies to the salts of sodium and potassium, which are chemical compounds, make this manifestly untenable.

Hypothesis of Werner.

In the case of water of crystallization and compounds like the double salts, the common view of an invariable valence made some explanation like that of molecular combination necessary. As a substitute for this and indeed for the valence idea, Werner[1] offered the hypothesis of a coordination number. This coordination number was the limiting number which tells how many atoms can stand in direct union with another definite elementary atom independent of the valence number. This coordination number was 4 or 6 in the majority of cases. For instance, if we take the ferric chloride, it appears that the molecule $FeCl_3$, although saturated, possesses still the power to unite with the molecule KCl, also saturated, to form the compound $FeCl_3.3KCl$.

Now, it is assumed that in this compound, the holding together of the molecules is determined by the fact that the iron atom even after the saturation of its 3 bonds has the power of entering into direct union with 3 more negative radicals. It is also assumed that in the above compound all 6 chlorine atoms are united with the iron atom; that in it a radical, $FeCl_6$, is present whose existence finds its explanation for the characteristic of iron to stand in direct union with 6 atoms, in the coordination number 6. The coordination number therefore brings to view a characteristic of the atoms which renders it possible to refer the so-called molecular compounds to actual union between definite atoms.

Werner explains, by the consideration of space relations,

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[1] *Ztschr. anorg. Chem.*, **3**, 267.

why the number 6 plays so important a rôle. If one assumes the atom to be a material point, and that the others directly combined with it are found upon a sphere described about the chief atom, then, since the space is limited, only a definite number of atoms can find place there so as to preserve a stable equilibrium. This limiting number is the coordination number. If it is 6, then the simplest assumption is of an octahedral arrangement. For 4, the symmetrical position is that of a plane. This coordination number, therefore, is connected with the space which the atoms occupy and has nothing to do with the valence, which remains unchanged. In the compound mentioned above, the iron atom remains trivalent and the 6 chlorine atoms together sexivalent. It is not necessary to follow the hypothesis as further elaborated by Werner.

Nitrogen Both Trivalent and Quinquivalent.

The following ingenious proof is cited by Remsen[1] to show that nitrogen may be both trivalent and quinquivalent, or that ammonium chloride and analogous compounds of nitrogen are true atomic and chemical compounds. If NH_4Cl is a molecular compound, then, as was explained above, two forces are concerned in the formation of its molecule.

1. A force holding together the nitrogen atom and 3 hydrogen atoms forming the molecule NH_3, and the hydrogen atom and chlorine atom forming the molecule HCl.

2. A force holding together the molecule NH_3 and the molecule HCl.

If these two forces are distinct in character the resulting molecule may be represented by the formula $NH_3 + HCl$. Suppose now we add together two other

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[1] *Loc. cit.*, p. 95.

molecules such that, taken together, their constituent atoms are the same in number and quantity as those contained in the compound $NH_3 + HCl$. Then the resulting compound ought not to be identical with that obtained in the former case. If these new molecules are, for instance, NH_2Cl and H_2, then the compound will be $NH_2Cl + H_2$ and this should not be identical with $NH_3 + HCl$ although its composition is exactly the same.

This method of investigation has been applied to the study of the problem under consideration, not indeed with the molecules employed in the above explanation but with molecules analogous to them. Instead of NH_3 the analogous compound $N(CH_3)_3$ was taken and this was united with C_2H_5I. Thus a compound was obtained which, if it be molecular, should be represented by the formula $N(CH_3)_3 + C_2H_5I$. Again, the compound $N(CH_3)_2C_2H_5$ was taken and this was united with CH_3I, yielding a compound which, as in the former case, should be represented by the formula $N(CH_3)_2C_2H_5 + CH_3I$. Now these two compounds ought not to be identical if they are molecular and not atomic. On comparing them, however, they were found to be in every respect identical. From this experiment it is concluded that the compounds studied are atomic compounds and that in them nitrogen is quinquivalent. The assumption of molecular compounds is, therefore, unjustifiable in most cases and unnecessary.

Saturated and Unsaturated.

Abandoning the hypothesis of two different combining forces to account for the variation in valence, another supposition has been that an atom in combination could be either saturated or unsaturated. When combined with the largest possible number of atoms it was considered saturated; with a smaller number it was unsaturated. The test for saturation was to see whether an atom in combination could unite with more atoms. Thus, in PCl_3 phosphorus is unsaturated as it has the power of taking on two more chlorine atoms, forming PCl_5. In CO carbon is unsaturated as it can combine with another oxygen atom, giving the compound CO_2. This idea was further confused with that of completeness. In PCl_5 the phosphorus atom was regarded as complete, in PCl_3 as incomplete. It is manifest that these names are an inheritance from the old phrase *saturation capacity* and that they carry with them ideas and analogies which have no basis in fact. It is safer and simpler to speak of phosphorus in the first case as quinquivalent and in the second as trivalent, and the carbon as bivalent and quadrivalent. No regularity is to be observed as to stability. Sometimes the compound in which the maximum valence is shown is the most stable and sometimes the one with the lower valence. It is not easily settled in many cases as to which is the typical valence unless a count of the compounds known be accepted as the criterion. It is now generally accepted that most elements occur in compounds with widely varying valence, some with three or four different valences.

Bonds or Links.

The necessity has been felt for the introduction of a term to indicate the influence exerted in holding one atom in union with another. Where the ignorance is so great as to the nature of this union, it is natural that much difficulty should be experienced in selecting a suitable term. Care must be exercised to avoid conveying ideas outside of present knowledge. The term *affinity* has been used. Thus a univalent element has one affinity, a bivalent has two, etc.

A serious objection to this is the confusion with the name for the combining force, which, as has been shown, is quite different. Affinity determines the fact that the atoms combine at all and not the number of atoms which combine. *Links* and *linkage* are terms associated with specific material union. Perhaps the best term is *bonds*. A quinquivalent element has 5 bonds. Too material a picture of this union should be avoided, and it must always be remembered that what we are attempting to picture is the emanation or exertion of some immaterial force or influence between two bodies in conjunction with one another. The various names are mentioned here, because they have each been largely made use of in the literature of the science. The term *valences* has also been used as synonymous with *bonds*.

Equality of Bonds.

It has been asked whether all of the bonds of an element are of the same order and represent equal exertions of force. It has been supposed, for instance, that phosphorus has three stronger bonds and two weaker, and so too for nitrogen, because the trivalent compounds were more stable than the quinquivalent. This mode of reasoning manifestly will not apply when the compound with the maximum valence is the most stable. Nor is it substantiated by experiment. It can be shown that the 5 bonds of nitrogen are all alike and equal so far as the most delicate methods of observation go. In the case of carbon this has been investigated with great care and the same conclusion reached. There are some grounds for thinking, that this is not true for all elements and, of course, the possibility exists that more delicate methods would reveal differences in all the elements. It should be added, however, that Werner regards the valences as differing in value. He speaks of the three primary valences (Hauptvalenzen) of nitrogen and the two secondary valences (Nebenvalenzen).

Self-saturation.

An extension of the hypothesis of saturation and unsaturation was the hypothesis of self-saturation, or, as it was sometimes called, re-entrant bonds. Two bonds of the same atom were supposed in some way to act upon each other, causing saturation. This gave what was considered a complete compound having no free bonds. This self-saturation was supposed to be easily overcome, and then other atoms held in combination. The basis for this lay very largely in the observation that the difference between the number of bonds was two. There would seem then to be two "latent bonds." While this is usually the case, and we have elements which are bivalent and quadrivalent and others trivalent, quinquivalent and septivalent, it does not seem to be at all a necessity. Some elements are bivalent and trivalent, etc. The assumption of self-saturation really explains nothing and is unnecessary. And so too, the hypotheses of double and triple linkage add nothing of value to chemical theory. There are undoubtedly different conditions of union, and these may be retained as convenient names devoid of theoretical significance.

Radical Change in Valence.

It is well to recognize that the change in valence is often a most radical and far-reaching one, influencing deeply what are ordinarily regarded as the chemical properties. Thus the change of univalent copper into bivalent, of univalent mercury into bivalent, of univalent gold into trivalent, of bivalent iron into trivalent, etc., gives distinct series of salts, cuprous and cupric, mercurous and mercuric, aurous and auric, ferrous and ferric, etc., differing almost as widely from one another as if they were formed from different elements. So pronounced is the difference, in fact, that Mendeléeff placed certain of them, as cuprous and cupric copper, in different groups in his system. And this is in one sense really justified, for an examination will show that according to chemical properties univalent copper belongs to the first group, and bivalent to the short iron group, or to the second group, etc. A large number of elements, positive and negative, form these different classes of salts on changing valence. This property has not so far been successfully deduced or connected with the ordinary periodicity of the elements, nor does it seem wise to attempt to arrange the elements exhibiting it under two or more groups in the system, as was attempted by Mendeléeff. Such a device would produce confusion and lead to no better understanding of the phenomenon. It is sufficient at present to point out the grave significance of the change.

Causes of Change in Valence.

The variability of valence must be accounted for in any theory as to the nature of valence and is a most important clue to the solution of that problem. It is necessary then to look closely into the agencies and conditions bringing about these changes.

Changes Caused by Light.

It is a matter of common observation that light can bring about physical, and the most varied chemical transformations. In some cases it causes a change of valence and this change may be either from a higher to a lower valence or *vice versa*. Thus certain mercurous compounds can be changed to mercuric, that is, univalent to bivalent.

$$Hg_2O = HgO + Hg.$$

An alcoholic solution of ferric chloride is changed by light to ferrous chloride, a change of trivalent to bivalent.

$$2FeCl_3 + C_2H_6O = 2FeCl_2 + C_2H_4O + 2HCl.$$

Ferric oxalate under the influence of light gives off carbon dioxide and becomes ferrous oxalate.

$$Fe_2(C_2O_4)_2 = 2Fe(C_2O_4) + 2CO_2.$$

An alcoholic solution of cupric chloride becomes cuprous chloride. Mercuric chloride in aqueous solution is slowly changed to mercurous chloride when exposed to light.

$$2HgCl_2 + H_2O = 2HgCl + 2HCl + O.$$

Auric chloride in contact with organic substance when exposed to light is changed first to aurous chloride and then to metallic gold.

Now the chemical action of light is generally attributed to the vibrations set up among the molecules. Rays having the shortest wave-lengths and the greatest frequency are most active in this respect, though all the rays of the spectrum have been shown to exert some action.

Changes Caused by Heat.

Variations in valence are very frequently caused by heat. These are commonly from a higher to a lower valence and are classed as dissociation phenomena. Thus cupric chloride becomes cuprous chloride.

$$CuCl_2 = CuCl + Cl.$$

Mercurous chloride is temporarily changed into mercuric chloride, the mercurous reforming on cooling.

$$2HgCl = Hg + HgCl_2.$$

Phosphorus pentachloride becomes the trichloride.

$$PCl_5 = PCl_3 + Cl_2.$$

Arsenic pentoxide becomes trioxide.

$$As_2O_5 = As_2O_3 + O_2.$$

An interesting series of changes are those in the sulphur chlorides. Thus sulphur tetrachloride (SCl_4) becomes sulphur bichloride (SCl_2) if warmed above —22°, and this becomes sulphur monochloride (S_2Cl_2) if heated above 64°. This last can be boiled without change. These instances might be multiplied, but it is not necessary.

The most plausible explanation offered as to the effect of heat in bringing about chemical change is a change in the velocity of vibration. Thus, L. Meyer[1] says, "If, therefore, the atoms composing a molecule are in motion, it is evident that they, by continued accelerated movement, may, at last, be so far removed from one another as to escape entirely the force of affinity, active only within narrow limits, and be unable to return within the sphere of its action."

Changes Caused by Electricity. Changes of valence due to electricity are not unusual. Thus we have the production of carbon monoxide from carbon dioxide by the passage of the electric spark.

$$CO_2 = CO + O.$$

In general such changes may be attributed to chemical action induced by the electricity serving as the direct agent. The change may be the result of changed vibration or to changes of electrical state.

Changes Caused by Chemical Action. The most usual method of bringing about a change of valence is by chemical action. These changes are frequently very complex. As meager as our present knowledge is, it does not seem to be a very hopeful task to enter the maze of changes of valence through chemical reactions with a view to clearing up the ideas as to the

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[1] "Modern Theories of Chemistry," London, 1888, p. 379.

nature of valence. A few examples may be taken. When manganese in a septivalent state and iron in a bivalent state come into the same sphere of action, the manganese is changed from its highest valency to its lowest and the iron from its lowest to a higher.

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

The simplest explanation would seem to be that these vibrating systems are unstable in the presence of one another. Bring together the three systems, $FeCl_3$ H_2SO_3 and H_2O,

$$2FeCl_3 + H_2SO_2 + H_2O = H_2SO_4 + 2HCl + 2FeCl_2.$$

Whether we are dealing here with a play of affinity, which causes the tumbling down of certain molecules and building up of others, or whether it is a question of vibratory equilibrium between these molecules cannot yet be told.

Hypothesis of van't Hoff.

Various hypotheses have been suggested to account for this property of the atom known as valence. First in point of time is the hypothesis of van't Hoff.[1] This is based upon the supposed form of the atom, and, like most of the other hypotheses, arose from a consideration of the carbon atom and its compounds.

"The simplest observation teaches that each change from the form of the cube must lead to greater attractions in certain directions since the atom can be more nearly approached, as it were, in these spots. Each form of that kind determines, therefore, a certain number of valences or chief powers of attraction. Where the nature of the united atoms determines the attracting power, the number also of the valences exhibited will be dependent upon

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[1] "Ansichten über die org. Chem.," I, 3.

it, and hence in comparing the compounds of a certain element with various others a variation in valence will often appear.

"If an atom moves equally in all directions, hither and thither, about a definite position, a change in the outer form and, along with that, in affinity and valence is a necessary consequence. When one considers that the length of the vibration of the atom's movements is determined by the temperature, the above view leads to the experimentally supported conclusion that increase of temperature lowers the number of the valences and weakens the exhibition of affinity; in other words, gradually reduces the interaction of the atoms to simple gravitation phenomena. The fact is that a higher temperature limit exists beyond which chemical action is no longer possible. And it is also a fact that on lowering the temperature the chemical action becomes very complex, which is without doubt to be attributed to the overlooked valences which in this way become active.

"An immediate consequence of these observations is that a molecule made up of atoms changes in the same fashion as the atom itself, only less sharply, and that the molecule has affinity and valence, which, indeed, are not inherent and peculiar to it, but are determined by its particular composition. This will account for the so-called molecular compounds."

Ostwald's Views.

This hypothesis is commented upon by Ostwald.[1] "There remains still a possibility of explaining the actual difference in the working of valence. If we look upon valence as a question of the characteristics of the atoms, whose action can be modified by the difference of condition of the atom,

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[1] "Lehrb. d. Allg. Chemie," [1], I, 830.

especially the condition of motion, then it is thinkable that while the cause of valence is unchangeable, the workings of this cause, even the valence itself, may seem different from time to time.

"An hypothesis of this kind has in fact been put forth by van't Hoff. In that he assumed that the chemical attraction between the atoms is a consequence of gravitation, he showed that if an atom possessed a form varying from that of the cube, the intensity of the attraction upon its surface must possess a fixed number of maximum attractions, which depends upon the form. The maxima can be of different value. If the motion of the atom due to heat is rapid, then only the greatest attractions can retain their atoms and the valence shows itself to be smaller by higher temperatures than by lower, which accords with experience."

This hypothesis involves a consideration of the form of the atom, and the assumption that the attracting force is exerted as a maximum in certain directions, towards the centers of the bounding faces, let us say. As these faces may be unequally distant from the center, these maxima may be unequal. The valences then or bonds will vary except in the case of such figures as the cube and the sphere. It would appear that there should be as many maxima or valences as there are sides, which would give a very large number for most geometrical forms, which is scarcely justified by experimental observations even at low temperatures.

Lossen on Valence.

Lossen's[1] idea as to valence, deduced from the consideration of the hypothesis of van't Hoff and Wislicenus as to the space relations of the atom, seem to be condensed into the single

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[1] *Ber. d. chem. Ges.*, **20**, 3309.

sentence : "This view leads, in my opinion, necessarily to the assumption that the polyvalent atom is not to be regarded as a material point, but that rather parts of it are to be differentiated from which the influence upon other atoms goes forth.

Wislicenus on Valence.

Wislicenus[1] expresses his ideas as to valence as follows : "I consider it not impossible that the carbon atom is a structure which in its form, more or less, perhaps very closely, resembles a regular tetrahedron, and further, that the causes of those workings which exhibit themselves in the so-called units of affinity (or bonds) concentrate themselves in the angles of this tetrahedral structure. These are possibly similar, and for analogous reasons, to the electrical working of a metallic tetrahedron charged with electricity. The bearers of this energy would finally be the primal atoms, just as the chemical energy of the compound radicals is undoubtedly a resultant of the energy dwelling in the elementary atoms."

Hypothesis of Victor Meyer and Riecke.

The following hypothesis has been advanced by Victor Meyer and Riecke :[2] "We have pictured to ourselves the following representation of the constitution of the carbon atom upon the basis of chemical and physical observations. We suppose this to be surrounded by an ether envelope which, in the case of isolated atoms, has the spherical form as they themselves have. The atom itself we regard as the bearer of the specific affinities, the surface of the envelope as the seat of the valences. Each valence we conceive as determined by the presence of two opposite electric poles which are fixed in the ends

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[1] *Ber. d. chem. Ges.*, **21**, 581.

[2] *Ibid.*, **21**, 951.

of a straight line, small compared with the diameter of the ether envelope. Such a system of two electric poles is designated as a double pole or 'dipole.' Four such dipoles would correspond to the four valences of the carbon atom. We think of the middle points of these as bound to the surface of the ether envelope but easily pushed into this. The dipoles turn freely about their centers." It is scarcely necessary to give the further assumptions.

Hypothesis of Knorr.

The hypothesis of Knorr[1] may also be given in brief. He pictures the valences, or bonds, as determined by a division of the atoms into special masses, discrete and separate, which he calls "valence bodies" (Valenzkörper). Each of these valence bodies possesses the power of attracting other valence bodies and of being fixed by this attraction. The atomicity is determined by the relative number of the valence bodies present in an atom. Union takes place through the contact of the valence bodies. In the carbon atom the valence bodies must be of equal value and symmetrically placed.

Hypothesis of Flawitzky.

Flawitzky[2] takes as a basis for his hypothesis the suggestion of N. Beketoff that the cause of the chemical interaction of the elements lay in the interference or coincidence of the motions of the atoms. The chief assumption is that the atoms of each element described closed curves which lie in planes which are parallel to one another and have a constant absolute position in space. The atoms of different elements move in planes which make definite constant angles with one another. If one

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[1] *Ann. Chem. Pharm.*, **279**, 222.

[2] *Ztschr. anorg. Chem.*, **12**, 182.

considers the active force of the atoms of different elements to be of equal magnitude, then the motion of an atom of one element can be completely counteracted by the motion of an atom of another element only when the two planes of motion are parallel to one another. Otherwise it can happen, according to the size of the angle between the planes of motion, that an atom of 1 element may require 2, 3 and more atoms of another to balance or equal it. In such cases only those components come into action which are parallel to the plane of motion of another atom. In accordance with this, the valence of an element may be referred to the difference in the angles between the path planes of the different atoms. The magnitudes of these cycles must apparently follow the law of quite rational relations by which is determined the capacity of the atoms to combine in whole numbers.

Kekulé's Views.

According to Kekulé,[1] valence is purely a kinetic question and is determined by the relative number of impacts which 1 atom receives from other atoms in a unit of time. In the same time in which the univalent atoms of a double-atomed molecule impinge once, at the same temperature the bivalent atoms in a double-atomed molecule come twice into contact.

Other Views.

There have been several attempts[2] at a mathematical solution of the problem of valence. Sedgwick's[3] contribution is a mechanical one and, as Hinrichsen remarks, reminds one of the view expressed by Lemery in the 17th century that the combining bodies possess, respectively, pores and points and that

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[1] *Ann. Chem. Pharm.*, **162**, 77.

[2] Jaumann: *Monatsh. Chem.*, **13**, 523; Gordon and Alexejew: *Ztschr. phys. Chem.*, **35**, 610.

[3] *Chem. News*, **71**, 139.

the compound is formed by these points entering the pores.

Hypothesis of Richards.

According to Richards,[1] the valence of an element is probably connected with its compressibility, since in general the greater the compressibility, the less is the valence. This relationship is explained with the help of the hypothesis assuming that atoms are compressible and elastic throughout their whole substance. The carbon atom, with small atomic volume and compressibility, would naturally possess high valence, and 4 larger atoms on combining with it would distort it into the tetrahedron demanded by the theory of van't Hoff and Le Bel. The disposition of the 4 added atoms on the faces, instead of the points of the tetrahedron thus formed, would of course make no difference in the geometric relation. If the 4 added atoms were all different, they would give an asymmetric distortion of the carbon atom.

Hypothesis of Venable.

According to Venable[2] there is no necessity for the assumption of a new force nor any hypothesis as to the forms of the atoms, the ether envelope, primal atoms, valence bodies, etc. The question whether the atoms of two elements will unite is decided by affinity. The kinetic theory supposes a motion of these atoms in the molecule. While one speaks of union, there is no actual contact to be assumed. The individual atoms have their own motion and, at the same time, the aggregation of atoms, or molecule, has a motion proper to it. In such a molecule we can infer from chemical reasons that there are one or more systems, depending upon the complexity of the molecule in which

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[1] *Science*, **16**, 283.

[2] *J. Am. Chem. Soc.*, **21**, 192, 220,

1 atom is "united" with 1 or 2 or more atoms. The conditions of equilibrium in such a system determine whether 1 atom or 2 or more atoms shall be "united" with a single atom. Two factors may be considered in this equilibrium, the peculiar motion of each elementary atom and the rate of motion dependent upon external conditions. The latter is readily changed by such agencies as heat, light, etc., and the valence will vary with the change in this factor.

There is then no distinct force of valence inherent in the atoms. The atomic weight has little influence in determining the number of atoms needed to satisfy the conditions of equilibrium except that there seems to be a general rule that with increase in the atomic weight in any one group more stable equilibrium is brought about with the smaller number of atoms, and in a choice between several the lesser valence is preferred. (Compare nitrogen and bismuth ; sulphur and selenium.)

A phosphorus atom unites with chlorine atoms because of a certain affinity between them. The number of chlorine atoms with which it will unite depends upon the possibility of an equilibrium, harmonizing the respective motions. As the temperature may impart a more rapid molecular motion, it is evident that the harmony, or equilibrium, will depend more or less upon the temperature and that a temperature may be reached at which no 2 or more atoms can remain in equilibrium, and hence no compound can be formed. The phosphorus atom, above mentioned, can, as we know, form a stable molecule with 5 atoms of chlorine. On increasing the temperature this becomes unstable and only 3 atoms can be retained. Neither with 4 atoms nor with 2 does there seem to be harmony of motion.

It is manifest that with this view there is no necessity for any assumption as to atomic and molecular combination nor for Werner's coordination number. As there can be an equilibrium determined by the motion of single atoms, so there can be an equilibrium of molecules determined by their motion. Thus the copper sulphate molecule moves in equilibrium with 5 molecules of water, an equilibrium readily disturbed by heating.

There may be sets of conditions bringing about harmony of motion. Thus a carbon atom moves in harmony with 4 hydrogen atoms or 2 oxygen atoms or 1 oxygen atom. Valence is a necessary sequence of the kinetic theory applied to atoms. This matter will be referred to again at the close of the last chapter.

CHAPTER VIII.

Molecules and the Constitution of Matter.

CHAPTER VIII.

MOLECULES AND THE CONSTITUTION OF MATTER.

We come, at the close of this discussion, back to the original question. How is matter constituted? All experimental research has brought support to the atomic theory of Leucippus in so far as that maintains that matter is composed of separate, discrete particles. These are, in their first analysis, not the atoms of Leucippus nor yet those of Dalton, but compound molecules. Matter, to the best of our knowledge and belief, is made up of molecules which are separable into their component atoms but which, within all ordinary experience, exist as complexes. In this it should be borne in mind that we are simply refining upon and elaborating Dalton's theory, which made little distinction at first between atom and molecule. Whether the term atom in its ancient meaning of the indivisible particle can be applied to the atoms of Dalton and of modern chemistry has after all slight bearing on the theory, and, whatever interest the solution of the question may have in itself, it can safely be neglected so far as the theory explaining the great laws of chemistry is concerned. To the mind of the chemist of to-day the elementary atoms are almost surely complex, but he cares little for that in the actual application of his theories. The truth is, that beyond certain properties, such as the physical one of weight, meaning the attraction of gravitation upon it, little is known concerning the elementary atom. Except in a few cases, such as the monatomic gases like mercury, the isolated, individual atom cannot at present be subjected to study, and practically little is known as to its behavior. In all dealing with matter, it is the molecule that comes under observation, and experience has taught that the atom is profoundly influenced in properties by the presence of other atoms. As has been shown, even in simple elementary gases the belief is justified that one is dealing with two-atomed molecules. In other gases this is more complex, and we can reason that the complexity greatly increases as we go from gases to liquids and from liquids to solids (although this has been denied), finding molecules more and more complex and nowhere the individual atom.

The Influence of Atom upon Atom.

If the body called hydrogen, which is known in the molecular condition to possess certain properties, is brought within the sphere of influence of the body called oxygen, whose properties in the molecular condition are also known, and the proper conditions of temperature are observed, union takes place, and a molecule of water is formed. This molecule of water contains one atom of oxygen and two atoms of hydrogen. The properties which characterized the molecule of hydrogen and the molecule of oxygen have entirely disappeared, and new characteristics appear, different from the former and in no known way connected with them nor derived from them. This change of properties is observed in all cases of chemical union, and is taken as indicative of the fact that chemical union has taken place. On decomposing the compounds and restoring the constituents, the former properties reappear ; therefore, they were merely cloaked, or rendered potential, with the tendency to their restoration persisting. A few properties, such as the atomic weight, are persistent and are not changed nor cloaked by the act of combination.

This behavior must be taken as indicating the profound influence exerted by one atom upon the other. No solution of the problem seems possible until the origin of the properties of an atom is known. It is scarcely conceivable that these properties are in a literal sense dependent upon the atomic weight, which is nothing more than the attraction exerted by the earth upon the individual atom. They vary with the atomic weight, or reversing the view, the atomic weight varies with them. As has been stated, the periodic system should not be looked upon as an arrangement solely according to the atomic weights, but according to all of the properties.

Nascent State.

The only opportunity, so far known, of observing the atom in the condition of freedom from union with other atoms is at the moment of its liberation from a molecule and before its entering into combination in a new molecule. This has been called the *status nascendi* or nascent state of the atom. The interval is undoubtedly exceedingly brief, and affords little opportunity for the observation of properties. The only one which has been noted with any degree of certainty is the far greater chemical activity of the free atom. One cannot be sure that he is dealing with the free atom, and mistakes have been made. It appears, however, that hydrogen just liberated has a power of breaking up existing molecules and making new combinations, which is not shown by molecular hydrogen. Thus the stable arsenic trioxide is broken up and compounds of arsenic and hydrogen, and oxygen and hydrogen formed, so too with antimony trioxide, nitric acid, nitrobenzol and many other compounds. The same increased reactivity has been noted in the case of nascent oxygen and other elements. What changes there are in other properties when the elements are in the atomic state can only be surmised.

Allotropism. Something may be inferred from what has been called the allotropic condition of an element. A number of the elements are known to exist in more than one form. Thus there are three well-known forms of carbon, several of sulphur, of phosphorus, of silver, of gold, etc. As only one kind of atom can be considered under each heading, the only plausible explanation is that there are molecules containing different numbers of atoms. A familiar example is that of oxygen and ozone. From a number of different reasons, we can infer that in oxygen the molecule has two atoms and in ozone three. These two forms of oxygen differ practically in all properties, chemical and physical, although the constitutional difference between them is so slight. When we come to consider allotropism in the case of most other elements, no method has been devised for telling the number of atoms in the molecules: we find them very different, and must assume that the numbers of atoms differ. As these atoms are all similar, the question of their arrangement in the molecule has not been considered as a factor, though unquestionably it may be one. The difficulties attending any investigation along this line are apparent. The fact remains, however, that the presence of two or more atoms of the same kind also materially influences their properties and confers new properties upon the molecule.

Further Cases of Atom Influencing Atom. The vast number of compounds which exist afford any number of examples of atom influencing atom, but two or three special cases may be taken which have a somewhat peculiar interest. Thus, the properties of molecular carbon are fairly well-known in the three different forms in which it exists. When it enters into a molecular arrangement with hydrogen, these properties are profoundly modified and new ones appear. The different molecules which can be formed with varying numbers of atoms of carbon and hydrogen are exceedingly numerous. In these, some properties persist, such as atomic weight, and atomic heat, but other properties are quite new. Thus we have CH_4, C_2H_6, C_6H_6, C_5H_8, $C_{14}H_{16}$, etc. When one other element is introduced, namely oxygen, we have proportions and properties almost as diverse as the organic nature surrounding us.

In the case of certain of these hydrocarbons, we have homologous series with a regular increment of carbon and hydrogen atoms. Thus there is the methane series, CH_4, C_2H_6, C_3H_8, C_4H_{10}, etc., or the ethylene series, C_2H_4, C_3H_6, C_4H_8, C_5H_{10}, etc. Here the changes of properties may be approximately predicted. In other words, the effect of adding a molecule, CH_2, is understood. The same effect is not always produced, but it depends upon the series into which it is introduced and the size of the molecule. Again, the differences are very noteworthy when the carbon atoms are under the influence of all the hydrogen atoms with which they can form stable molecules and when the hydrogen atoms are less than is demanded for such perfect harmony.

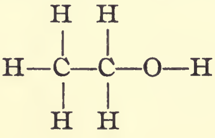
Isomerism. Again, different properties are produced when the same atoms are differently arranged. A great many compounds are known which have the same elements, the same ratio between them and the same molecular weight, or the same number of atoms in the molecule. Thus, two substances are known having the formula C_4H_{10}, three having the formula C_5H_{12} and five having the formula C_6H_{14}. No other plausible explanation is offered of the existence of these bodies other than that they have the atoms in the molecules differently arranged. This is called isomerism. The difference may be comparatively slight, as in the case of the three mesitylenes C_9H_{12}, or very great, as in the case of dipropargyl and benzol, C_6H_6, thus indicating a greater or lesser difference of arrangement.

The arrangement of the atoms in a molecule then has a most important influence upon the properties of the molecule. The most plausible explanation of this is in the assumption of intramolecular motion modified by the changed atomic and molecular motion and the modifications produced by the necessity for harmonizing these motions in a system.

Influence of Position.

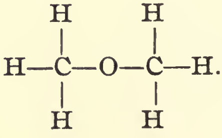
It is, furthermore, a well-known fact of chemistry that the relative position of the atoms has a most important bearing upon the properties of the molecule. These are in reality somewhat more complex cases of isomerism than those mentioned in the last paragraph,—substances containing more than two elements yet having the same elements, the same ratio and the same molecular weight and showing different properties. Thus we have two bodies with the formula C_2H_6O. Chemically and physically they are absolutely unlike. They cannot be classed together at all. Many reactions, decompositions and syntheses lead to the conclusion that in one case we have two groups of atoms, C_2H_5 and OH, united by one of the carbon atoms, and in the other two groups, CH_3 and CH_3, united by an atom of oxygen. The two formulas then are written $C_2H_5.OH$ and $CH_3.O.CH_3$, or graphically

(1)



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$$

and (2)

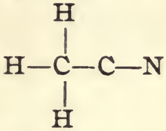


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}O{-}\overset{H}{\underset{H}{C}}{-}H.}$$

The relative position of the atoms in (1), wherever it occurs, gives what is known as alcoholic properties. The relation observed in (2) gives the properties of ethers.

Two bodies are known with the formula CH_3CN. They are very different in properties. The conclusion reached is that we have to consider these

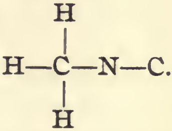
(1)



$$H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-C-N$$

and

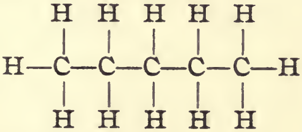
(2)



$$H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-N-C.$$

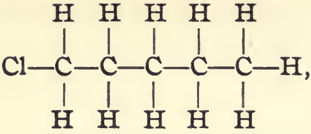
This is confirmed by many reactions and is no mere assumption. Thus the entire character of the molecule is decided by the relative position of the atoms of carbon and nitrogen as compared with the radical group CH_3. Again two bodies (1) C_2H_5SCN and (2) C_2H_5NCS are known. They differ in properties, and this difference leads to an assumption of a difference in arrangement of the atoms in the molecule. In (1) one carbon atom of the radical is united with the sulphur atom or in juxtaposition to it. In (2) the carbon atom bears the same relative position to the nitrogen atom.

Recalling other familiar examples from organic chemistry, we find that the union of an atom or group of atoms, as Cl or NO_2, to a carbon atom in a hydrocarbon which had three atoms in union with it, produces a different compound from that formed by the union with a carbon atom which had only two hydrogen atoms. Thus the hydrocarbon



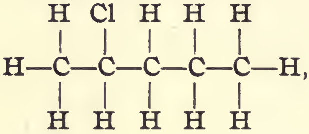
$$H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

can form two chlorides and two only.

(1) 

$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ Cl & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

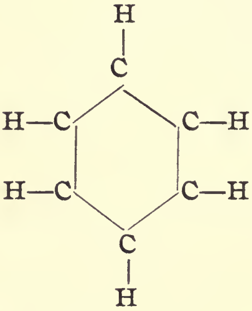
, primary amyl chloride;

(2) 

$$\begin{array}{ccccccccccccc} & & H & & Cl & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

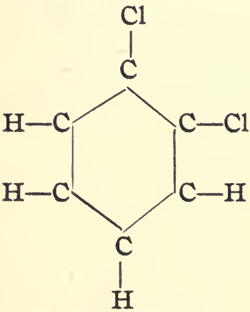
, secondary amyl chloride.

A different compound is produced according to the number of carbon atoms between two introduced atoms. Thus benzol,

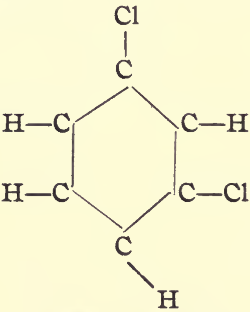


,

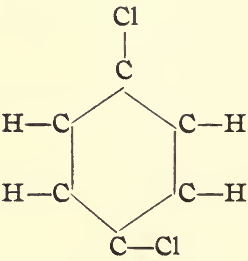
gives three dichlorides,



Orthochlorbenzol.



Metachlorbenzol.



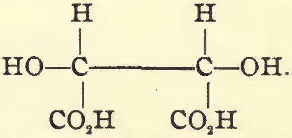
Parachlorbenzol.

This means that the interposition of one or two carbon atoms between those united with the chlorine brings about different properties.

It is not necessary to multiply examples further. It is sufficiently clear that the nature of a molecule is not merely dependent upon the number and character of the atoms composing it, but is deeply modified by their relative positions within the molecule.

Effect of Position in Space.

Certain cases of isomerism have been observed in which the differences between the bodies are physical. These are known as physical isomers, and the bodies are chiefly distinguished from one another by their action upon light. The usual explanation of the isomerism, namely, a different arrangement of the atoms as lying in one plane, is not possible in these cases. The Le Bel-van't Hoff theory would explain these atoms or groups as differently situated in space of three dimensions. Such cases have been observed only where an asymmetric carbon atom is present. Such an asymmetric atom is one which has each bond satisfied with a different group or atom. Thus tartaric acid has the formula



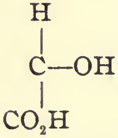
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ HO- & C & \text{———} & C & -OH. \\ & | & & | & \\ & CO_2H & & CO_2H & \end{array}$$

Four modifications of this acid are known: one polarizing light to the right, one to the left, one inactive form which can be resolved into the dextro- and laevorotary, and one which cannot be so resolved. Regarding the inactive form, which can be resolved into the two active forms, as a mixture or combination of the two, there are left three distinct forms to be accounted for.

The stereochemical explanation is usually given as follows: "The two immediate carbon tetrahedra, having a common axis and joined by one summit, have the three different groups arranged right or left. This would result in a dextro- and laevorotatary tartaric acid. If, however, the three side groups are arranged in opposite directions, their influence will cease and the product will be an inactive tartaric acid. This cannot be resolved."[1]

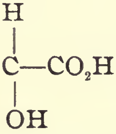
It may not be absolutely necessary to seek an explanation of this isomerism by supposing space relations outside of the plane surface. Manifestly in such a grouping there may be three different positions in the plane:

(1)



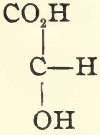
$$\begin{array}{l} \;\;H \\ \;\;| \\ \;\;C{-}OH \\ \;\;| \\ CO_2H \end{array}$$

(2)



$$\begin{array}{l} H \\ | \\ C{-}CO_2H \\ | \\ OH \end{array}$$

(3)



$$\begin{array}{l} CO_2H \\ \;\;| \\ \;\;C{-}H \\ \;\;| \\ OH \end{array}$$

Unless a difference be granted in the bonds these are the only three possible relations. If the kinetic theory is true, the changes in the harmonic motion of the molecule brought about by such transpositions might suffice to account for the slight changes in properties.

An Explanation in the Kinetic Theory.

How are these changes in the properties of the atom and molecule, pointed out in the preceding pages, to be explained? The most plausible explanation which has been given is found in the kinetic theory. Most, if not all, of the properties of the atom may be dependent upon its motion. This motion is more or less profoundly modified by bringing it within the sphere of influence of another atom or atoms, and the result is a molecule with harmonic molecular motion—a harmonized sys-

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[1] Richter's "Organic Chemistry," (Smith), p. 475

tem of motions evidenced by new properties. Release an atom or a group from this system, and the old motion is restored and the former properties reappear. Manifestly all changes of relative position or of grouping must modify the motion of the system and affect the properties. All reproductions of the same grouping will give the same effect. The introduction of an atom or group into harmonically different parts of the system will produce more or less distinctly different effects. Without the application of the kinetic theory, these phenomena are exceedingly difficult to explain.

Properties of Molecules.

It is impracticable in a work of this compass to discuss at length the properties of molecules as they have been worked out by the aid of modern mathematics and physics. It will have to suffice to enumerate such of these properties as seem to be more surely established. They are of profound interest and importance to science, but much of the work is still too hypothetical in nature. An important part of the work of the future will be the thorough grounding of these theories.

Molecular Motion.

A consideration of the general behavior of gas molecules, and especially under the influence of changes of temperature, led Herapath,[1] Joule,[2] Krönig[3] and Clausius[4] to announce and develop a mechanical theory of heat and a kinetic theory for gases. The kinetic theory is that the molecules of a gas are in incessant motion; this motion is in a straight line or path and of an unchanging velocity. This kinetic

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[1] Annals of Phil., 1821, pp. 273, 340, 401.

[2] Manchester Lit. and Phil. Soc., 1851, p. 107.

[3] Grundzüge einer Theorie der Gase, Berlin, 1858.

[4] Pogg. *Ann.*, **100**, 353.

theory is, in a measure, the old vision of molecular motion as seen by Greek philosophers and metaphysicians of the Middle Ages reduced to a mathematical basis.

These molecules meeting one another in their paths give rise to countless impacts. From the impacts, we have the pressure or tension of the gases. From this pressure the absolute velocity of the molecules has been calculated, and also from the rates of diffusion of the gases. The figures obtained show a very great velocity, differing with different gases. Thus the oxygen molecule is said to move at a rate equal to 461 meters per second and the hydrogen molecule 1844 meters per second at 0° C.

Properties of the Molecule.

While much work has been done to calculate the size of the molecule and the position of the component atoms in space with reference to the center of gravity, it cannot yet be claimed that much is definitely established. The conclusions of Meyer[1] are, however, of great interest. These calculations place the diameter of a hydrogen molecule at 1.84 millionths of a centimeter.[2] The number of molecules of air in a cubic centimeter under a pressure of one atmosphere[3] is placed at 60,000,000,000,000. It can be readily seen that it is impossible to entirely free any space of molecules of air by means of an air-pump. A large number of molecules will still be left. Indeed the number of impacts of any one molecule upon other molecules is calculated as being still 46,500 in a second in a volume of air reduced from the pressure of one atmosphere to that of 0.01 mm.[4] If all of the molecules in a cubic centimeter of air, at ordinary pres-

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[1] "Kinetische Theorie der Gase," pp. 299, 310.

[2] *Ibid.*, p. 333.

[3] *Ibid.*, p. 335.

[4] *Ibid.*, p. 213.

sure be spread out in a plane in close contact with one another, they would cover, along with their molecular spheres, a surface of 1.84 square meters.[1] In calculating the absolute weight of molecules, Meyer[2] calculated that 46,000,000,000,000 molecules of air weigh one milligram.

Experimental Investigations.

Efforts have been made repeatedly by older chemists and those of more modern times to determine the limits of divisibility of molecules. These have little value beyond a rough confirmation of the preceding numbers reached by mathematical methods. Thus Meyer records the experiment of A. W Hofmann[3] that coloring-matter can be readily detected in a dilution of $\frac{1}{100,000,000}$ and even greater; that is, the smallest weighable quantity can be divided several hundred million times. Annaheim[4] had in this way calculated that an atom of hydrogen must weigh less than 0.05 millionth part of a milligram. There is also an experiment by Kirchhoff and Bunsen,[5] which shows that the three-millionth part of a milligram of sodium chloride suffices to color a flame distinctly. Faraday[6] prepared gold leaf, the thickness of which was one hundred times less than the length of a light wave. Since this leaf must at least consist of a layer of atoms, the diameter of a gold atom must be equal to or less than five-millionths of a millimeter. As noted on a previous page, the gas theory gave as the diameter of a molecule one-fifth of a millionth of a millimeter. Röntgen[7] has shown

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[1] "Kinetische Theorie der Gase," p. 301.

[2] *Ibid.*, p. 337.

[3] *Ber. d. chem. Ges.*, 1870, p. 660.

[4] *Ibid.*, 1876, p. 1151.

[5] Pogg. *Ann.*, 1860, p. 168.

[6] *Ibid.*, 1857, p. 318.

[7] Wied. *Ann.*, 1890, **41**, 321.

that oil layers could be prepared having a thickness of only 0.56 millionth of a millimeter. A number of other experiments are cited by Meyer, in which the thickness of bubble-films, the weights of water films on glass, or the limits of capillary force were determined in the effort at settling the limits of molecular diameters. These approximations tend to confine the estimate given above.

Since the diffraction of light in the microscope prevents a clear definition of anything smaller than the one four-thousandth part of a millimeter, no direct use can be made of this instrument in the investigation under consideration. Still there are optical methods which have been used,[1] giving results that coincide well with those deduced from the theory of gases. Electrical methods have been used by Thomson, by Lorenz,[2] and by Oberbeck.[3]

Meyer draws the conclusion[4] that while these methods for determining the limit of divisibility of matter do not all yield similar results as to the size of the particles, yet they agree without exception in this that the thickness of a molecule of the material examined can not be less than the millionth part of a millimeter. He regards this as a fairly well-determined limit of size for the smallest particles.

It might be claimed that none of these methods give any direct proof of the existence of particles at all but simply concern the thickness of material. One experiment of Sir William Thomson would seem to meet this objection. This was referred to above.[1] The simple laws of dispersion in transparent substances could not be

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[1] W. Thomson in Exner's Report, **21**, 222 (1885).

[2] Pogg. *Ann.*, **140**, 644 (1870).

[3] Wied. *Ann.*, **31**, 337 (1887).

[4] Meyer: *Loc. cit.*, 342.

true if only a few particles were found in the path of a light wave. If there are many of these present, then the distance between two neighboring molecules must be much smaller than the length of a light wave. If the number of these is 1,000, then we get for the value of the distance 0.000,000,5 mm., a number which agrees with that obtained from a consideration of the kinetic theory.

Divisibility of Matter

There still remains the old puzzle as to the divisibility of matter, or rather, as Meyer puts it, "as to the marvelous property of indivisibility." Something has been learned as to the size, weight, form and motion of the molecules. These we suppose to be made up of atoms, and no difficulty is experienced in separating them into their component atoms. There are indications that the atoms themselves are related, have some common constituents, and so are compound, but the problem of their division remains unsolved. The calculations just given as to their size would make it also extremely improbable that such relatively large bodies are really indivisible. Repeated efforts have been made to split up these atoms, but the lines of investigation have promised little and yielded nothing. There are, however, several hypotheses as to the nature of atoms which are of interest, though of course little weight can be attached to them in their unsupported condition.

Rankine's Hypothesis.

This hypothesis was attributed by Rankine[1] to Sir Humphry Davy. Rankine was, however, the first to develop it by mathematical methods. It is an hypothesis of molecular vortices which assumed "that each atom of matter consists of a nucleus or central point enveloped by an elastic

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[1] *Phil. Mag.*, **10**, 354, 411 (1855).

atmosphere, which is retained in its position by attractive forces, and that the elasticity due to heat arises from the centrifugal force of those atmospheres revolving or oscillating about their nuclei or central points." Whether these elastic atmospheres are continuous or consist of discrete particles, Rankine does not attempt to decide.

Vortex Atoms.

The vortex theory of Thomson[1] is based upon a mathematical investigation of Helmholtz in which the vortex motion of a fluid in motion without friction was examined. If we take the rings of smoke, such as are sometimes observed, we shall find in them an illustration of the vortices. Helmholtz, assuming the fluid to be incompressible, homogeneous and without friction, proved by mathematical methods:

(1) That if such a vortex is once formed, it will continue to exist forever. It cannot be destroyed in such a medium, nor produced. It required an act of creation at the time of formation of the liquid.

(2) A vortex always consists of the same portion of the fluid. It is not mere motion in the fluid, but actual transference or traveling of the same portion of the fluid.

(3) No two vortices can occupy the same space nor intersect one another. A vortex must behave as a perfectly elastic body.

Other important deductions were made by Helmholtz, but these are the ones most directly applied by Thomson in his theory.

Thomson's Theory.

The theory of Thomson has to this extent connection with the Cartesian theory in that all space is supposed to be filled with continuous, homogeneous, frictionless matter which has the nature of a fluid and is like the ether of ancient and

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[1] *Phil. Mag.*, **34**, 15 (1867).

modern physicists. There is but this one kind of matter. Out of this continuous mass, small ring-like portions separate. These cannot separate because of any motion in the ether itself. They cannot be divided into parts, nor can they be destroyed by any force originating in matter made up of them. These vortices are the atoms of all ponderable substances, and between them lies the original ether. "The unchanging mass of these vortex atoms is determined solely by the condition of the motion in which the world found itself at its creation. The manifold character of these conditions had called forth manifold kinds of vortices, which, in spite of this, were built up of the same substance and according to the same laws, and which must bear witness to these laws for all time by the regularity of their characteristics. Thus would this theory make it possible to explain the obedience to law shown by the properties of the atoms, and especially to the law of the periodicity of these properties."[1]

In considering this theory Maxwell says:[2] "when the vortex atom is once set in motion, all its properties are absolutely fixed and determined by the laws of motion of the primitive fluid, which are fully expressed in the fundamental equation. The disciple of Lucretius may cut and carve his solid atoms in the hope of getting them to combine into worlds ; the followers of Boscovich may imagine new laws of force to meet the requirements of each new phenomenon, but he who dares to plant his feet in the path opened up by Helmholtz and Thomson has no such resources. His primitive fluid has no other properties than inertia, invariable density, and perfect mobility, and the method by which the motion of this fluid is to be traced is pure mathematical analysis. The difficulties of

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[1] Meyer, "Kinetische Theorie der Gase," p. 351.

[2] Encyc. Brit. Article Atom.

this method are enormous but the glory of surmounting them would be unique."

Properties of the Vortex.

These vortex-atoms must be perfectly elastic, even though the ether itself be devoid of elasticity. In the case of impacts, these atoms would behave in a manner similar to elastic bodies, and it is easy to see how light, swinging movements of the atoms would be transmitted to the ether and from the ether to the atoms. Thus an influence can be exerted by atom upon atom at a distance. Thomson and Tait,[1] Kirchhoff[2] and others have shown mathematically how rings and other bodies which are in a fluid in motion exercise an influence apparently comparable to an electrodynamic upon one another.

The vortex need not have the form of rings. The rings may be knotted (without intersection), or other forms can be supposed. Pulsating masses have been considered which, having a spherical or similar form, show an internal motion in which at any one point there are regular vibrations in a radial direction.

Consequences of the Theory.

It is by rigid mathematical analysis that the vortex theory and its consequences are to be worked out. It admits of few assumptions. It is most closely connected with the theory of electricity and light. It means not merely a kinetic theory of gases but of solids and liquids, of heat, light and electricity. The harmony of the universe is motion, and so at the close of more than twenty centuries we come back to a theory of a universe filled with a continuous matter, and, at the same time, an atomic theory. But the theory is no longer a baseless

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[1] Treatise on Nat. Phil., **1**, 264 (1867).

[2] Crelle: *Borchardt's Jour.*, **71**, 237, 263 (1870).

dream. It would seem to be the culmination of centuries of work, not fancy, and to embody the explanation of all facts known—chemical, physical and mathematical. There is still much to be done and many untrodden paths. The theory must yet stand many exacting tests, but so far at least nothing has been thought out which so satisfies the conditions known to us.

The Vortex Theory Applied to Valence.

It will readily be seen that Thomson's theory of vortex atoms agrees well with the kinetic equilibrium theory of valence and offers a satisfactory explanation of the difference between the atoms. In the case of a univalent atom, we have a vortex whose motion enables it to enter into harmonic motion with one other vortex, giving a stable molecule; for a bivalent atom, the motion is such that there can be unison with two of the former vortices or with one having a similar motion. This motion may be dependent upon the peculiar form of the vortex. Thus, elementary atoms of Group I might have one distinctive form and motion, of Group II another, and so on through Group IV, or possibly through Group VII.

A change of valence, which we have seen was so easily brought about by the action of another force, as heat or light, would mean a change of form and motion in the vortex. Thus a vortex with three knots might become a simple ring or a vortex having a different number of knots. It is evident, however, that there is some tendency to return to the original form and motion when the original conditions are restored.

The Vortex Theory and Affinity.

The motion of the vortex atom makes it a center of force. There is no force without motion. The motionless ether is without force. Weight, which is but one form of attraction, acting at a distance and dependent upon mass, is one of the results of this force. The ether is without weight. The properties of the atoms show a certain periodicity according to mass and weight, that is, are determined by the motion of the vortex; chemical affinity is another kind of attraction which must also depend upon the motion, and in some way may be related to the motion of electricity. What is meant by the union of atoms other than the joining of two or more vortices in harmonic motion is unknown to us, but the new motion of the harmonic system means, of course, new properties depending upon this motion. The dissociation of this molecule restores the old condition of motion and the properties dependent upon it. The laws of distribution of acids and bases in double decompositions and of mass action in general should afford valuable data for reducing to a rigid mathematical basis these questions of motion and form.

Electron Hypothesis.

J. J. Thomson has announced a hypothesis which, while referring more directly to force, has its bearing ultimately upon the constitution of matter. The basis of the hypothesis is decidedly debatable, presenting points which may not be generally admitted. The hypothesis itself is used to explain certain phenomena connected with electricity and those emanations of force or matter known as Röntgen rays, Becquerel rays, etc.

It is deduced[1] from Faraday's laws of electrolysis that the current through an electrolyte is carried by the atoms of the electrolyte, and that all of these atoms carry the same charge, so that the weight of the atoms required to carry a given quantity of electricity is proportional to the

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[1] *Pop. Sci. Monthly*, 1901, p. 323.

quantity carried. To carry the unit charge of electricity requires a collection of atoms of hydrogen which together weigh about 0.1 milligram. If the charge of electricity on an atom of hydrogen can be measured then one-tenth of this charge (numerically) will be the weight of the atom of hydrogen in milligrams. Thomson shows how this charge may be measured. To carry a given charge of electricity by hydrogen atoms requires a mass a thousand times greater than to carry it by the negatively electrified particles, which constitute the cathode rays, and it is very significant that while the mass of atoms required to carry a given charge through a liquid electrolyte depends upon the kind of atom, being, for example, eight times greater for oxygen than for hydrogen atoms, the mass of cathode ray particles required to carry a given charge is quite independent of the gas through which the rays travel and of the nature of the electrode from which they start. By a very ingenious method it seems possible to determine the electric charge carried by one of these particles. The conclusion is reached that the charge on one of these particles is the same as that on an atom of hydrogen in electrolysis. From this it follows that the mass of each of these particles is only about one one-thousandth part of a hydrogen atom. These negatively electrified particles Thomson calls corpuscles. They form an invariable constituent of the atoms or molecules of all gases, and presumably of all liquids and solids. These corpuscles seem to be given off by incandescent metals and by certain radioactive bodies. The carriers of negative electricity are these corpuscles of invariable mass. The carriers of positive electricity are connected with a mass, which is of the same order as that of an ordinary molecule and which varies with the nature of the gas in which the electrification is found. Thomson conceives that negative electricity consists of these corpuscles, and that positive electrification consists in the absence of these corpuscles from ordinary atoms. Negative electricity (*i. e.*, the electric fluid) has mass; a body negatively electrified has a greater mass than the same body in the neutral state; positive electrification, since it involves the absence of corpuscles, is accompanied by a diminution in mass. The idea that mass in general is electrical in its origin is a fascinating one to Thomson, although he acknowledges that it has not at present been reconciled with the results of experience.

Of course these corpuscles, if their existence can be surely maintained, have a most important bearing upon the constitution of matter. If his suggestions are true that electricity has weight and mass—that mass is electrical—then the ultimate conclusion is, that force occupies space and there is no matter. Force alone makes up the Universe.

It can only be said that satisfactory evidence is lacking and the conclusion unjustified at present.

Crookes' Summary.

The following summary by Crookes[1] is given in a condensed form here to show the views held by one who has taken a somewhat advanced stand in speculation as to chemical theory.

"For nearly a century, men who devote themselves to science have been dreaming of atoms, molecules, ultramundane particles and speculating as to the origin of matter. To show how far we have been propelled on the road, we have but to recall matter in a fourth state, the genesis of the elements, the existence of bodies smaller

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[1] *Science*, **17**, 993.

than atoms, the atomic nature of electricity, and the perception of electrons.

"In 1879 I advanced the theory that in the phenomena of the vacuum tube at high exhaustions the particles constituting the cathode stream are not solid, not liquid, nor gaseous, do not consist of atoms propelled through the tube and causing luminous mechanic or electric phenomena where they strike, but that they consist of something much smaller than the atom—fragments of matter, ultra-atomic corpuscles, minute things very much smaller, very much lighter than atoms—things which seem to be the foundation stones of which atoms are composed.

"In 1888 in connection with a theory of the genesis of the elements I spoke of an infinite number of immeasurably small ultimate particles gradually accreting out of the formless mist and moving with inconceivable velocity in all directions. I strove to show that the elementary atoms themselves might not be the same now as when first generated, that the primary motions which constitute the existence of the atom might slowly be changing and even the secondary motions which produce all the effects we can observe —heat, chemic, electric, and so forth—might in a slight degree be affected and the probability was shown that the atoms of the chemical elements were not eternal in existence, but shared with the rest of creation the attributes of decay and death.

"Another phase of the dream now demands attention. W. K. Clifford said in 1875: 'There is great reason to believe that every material atom carries upon it a small electric current, if it does not wholly consist of this current.'

"The idea of unit or atoms of electricity which has been contributed to by Faraday and others, took concrete form when Stoney showed that Faraday's law of electrolysis involved the existence of a definite charge of electricity associated with the ions of matter. This definite charge he called an electron. It was not till some time after the name had been given that electrons were found to be capable of existing separately.

"During my inaugural address in 1891 as president of the Institution of Electrical Engineers an experiment was shown which went far to prove the dissociation of silver into electrons and positive atoms. A silver pole was used and near it in front was a sheet of mica with a hole in its center. The vacuum was very high and when the poles were connected with the coil, the silver being negative, electrons shot from it in all directions and, passing through the hole in the mica screen, formed a bright phosphorescent patch on the opposite side of the bulb. Silver was seen to be deposited on the mica screen only in the immediate neighborhood of the pole, the far end of the bulb, which had been glowing for hours from the impact of electrons, being free from silver deposit. Here, then, are two simultaneous actions. Electrons, or radiant matter, shot from the negative pole, caused the glass against which they struck to glow with the phosphorescent light. Simultaneously, the heavy positive ions of silver freed from negative electrons and under the influence of the electrical stress likewise flew off and were deposited in the metallic state near the pole. The ions of metal thus deposited in all cases showed positive electrification.

"All of the isolated facts mentioned—ultragaseous matter, division of atoms, electrons, etc., are focused and welded into one harmonious theory by the discovery of radium. Let me briefly recount some of the properties of radium and show how it reduces speculations and dreams, apparently impossible of proof, to a concrete form.

"The most striking property of radium is its power to pour out torrents of emanations which are of three kinds. One set is the same as the cathode stream, now identified with free electrons. These electrons are neither ether waves nor a form of energy, but substances possessing inertia (probably electric). Liberated electrons are exceedingly penetrating. They will discharge an electroscope when the radium is 10 feet or more away, and will affect a photographic plate through 5 or 6 mm. of lead. They are not readily filtered out by cotton wool. They do not behave as a gas, but more like a fog or mist. They are deviable in a magnetic field. They are shot from radium with a velocity of about one-tenth that of light but are gradually obstructed by collisions with air atoms so that some become much slowed and then diffuse in the air and give it temporary conducting powers.

"Another set of emanations from radium are not affected by an ordinary powerful magnetic field and are incapable of passing through thin material obstructions. These have about one thousand times the energy of those radiated by the deflectable particles. They render air a conductor and act strongly on a photographic plate. Their mass is enormous compared with that of the electrons and their velocity is probably as great when they leave the radium, but in consequence of their greater mass they are less deflected by the magnet, are easily obstructed by obstacles and are sooner brought to rest by collisions with air atoms. These are affirmed to be the positive ions. Rutherford has shown that these emanations are slightly affected in a very powerful magnetic field but in an opposite direction to the negative electrons. He has measured their speed and mass and shown them to be ions of matter moving with the speed of the order of that of light.

"There is also a third kind of emanation produced by radium. These accompany the others. They are not at all affected by magnetism and are Röntgen rays—ether vibrations—produced as secondary phenomena by the sudden arrest of velocity of the electrons by solid matter.

"The actions of these emanations on phosphorescent screens are different. The electrons are much less penetrating than Röntgen rays. The power with which radium emanations are endowed of discharging electrified bodies is due to the ionization of the gas through which they pass. This can be affected in many other ways as by splashing water, red hot bodies, flame, etc.

"According to Sir Oliver Lodge's electronic theory, an atom of matter has a few extra negative electrons in addition to the neutral atom. When these are removed, it becomes positively charged. The negative charge consists of unbalanced electrons, one, two, three, etc., according to the balance.

"It is recognized that the electrons have the one property which has been regarded as inseparable from matter, namely inertia. In 1881 J. J. Thomson developed the idea of electric inertia (self-induction) due to a moving charge. The electron, therefore, appears only as apparent mass by reason of its electrodynamic properties, and if we consider all forms of matter to be merely congeries of electrons, the inertia of matter would be explained without any material basis."

Lodge on Modern Views of Matter.

In the Romanes Lecture for June 12, 1903,[1] Lodge has summarized certain views as to the nature of matter. He stated as his first thesis "generally accepted by physicists" that an electric charge possessed the fundamental property of matter, called mass or inertia, and that if a charge were sufficiently concentrated it might represent any amount of matter desired. There were reasons for supposing that electricity existed in such concentrated small portions, which were called electrons, and could either be associated with atoms of water, to form the well-known chemical ions or could fly separate as was observed in the cathode rays of vacuum tubes and in the loss of negative electricity when ultraviolet light falls upon a clean negatively charged surface. The hypothesis suggested on the strength of these facts is, that the atoms of matter are actually composed of these unit electric charges or electrons, an equal number of positive and negative charges going to form a neutral atom, a charged atom having one electron in excess or defect. On this view a stable aggregate of about 700 electrons in violent orbital motion among themselves would constitute a hydrogen atom, sixteen times that number would constitute an oxygen atom, and about 150,000 would constitute an atom of radium.

This hypothesis represents a unification of matter and a reduction of all material substances to purely electrical phenomena. Assuming this electrical theory of matter, that the atoms are aggregates of electric charges in a violent motion, two consequences follow. One of these consequences depends on the known fact that radiation or light or an ether wave of some kind, is emitted from

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[1] *Science*, 18, 122.

any electron subject to acceleration; consequently the revolving constituents of an atom must be slowly radiating their energy away, must thus encounter a virtual resistance and must in that way have their velocity increased.

The second consequence is that when the speed of an electrified body reaches that of light its mass becomes suddenly infinite; and in that case it appears not improbable that a critical condition would have been reached, at which the atom would no longer be stable but would break up into other substances. And recently a break-up of the most massive atoms has been observed by Rutherford, and has been shown to account for the phenomenon of radioactivity, some few of the atoms of a radioactive substance appearing to reach a critical stage at which they fling away a small portion of themselves with great violence, the residue having the same property of instability for some time, until ultimately it settles down into presumably a different substance from that which it was at the beginning.

Lodge's further hypotheses and speculations may well be omitted here.

Rutherford's Hypothesis.

It is, of course, impossible, in the present state of knowledge concerning the radioactive bodies and their strange emanations, to attach any serious value to the various guesses at a solution of the problems involved. The phenomena are so new and so remarkable that former experience can not serve us, and some of the older hypotheses or ideas as to matter and force will apparently require an overhauling and reformulation. In closing the subject Rutherford's suggestions[1] may be mentioned as at least interesting.

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[1] Rutherford: "Disintegration of the Radioactive Elements," *Harpers Mag.*, 1904, p. 280.

"The radiating power is thus an inherent property of the radioactive elements and must reside in the atoms themselves. Since the radiation consists of the projection of matter, this matter must be a part of the atom and the latter must suffer disintegration. Now it is impossible to imagine any mechanism possessed by the heavy atoms of the radioactive elements whereby they suddenly project from rest a portion of themselves with enormous velocity. It seems far more likely that the atoms themselves are very complex systems, consisting of smaller charged parts in rapid rotation and held in equilibrium by their mutual forces. For some reason the atom becomes unstable, and one of these parts suddenly escapes from the system with the velocity it possessed in its orbit. . . . The chain of substances that are being spontaneously produced from the parent element cannot be due to the breaking up of molecular systems but must arise from an actual disintegration of the atoms of the radioactive elements into simpler forms."

Clarke on the Atomic Theory.

It is easy to see that much of the speculation of the last few pages is based on very questionable evidence or altogether unsupported by fact. It is well to quote in conclusion the conservative words of Clarke in the Wilde lecture delivered on the centennial anniversary of the announcement of the atomic theory.[1] "If we take the atomic theory out of chemistry we shall have left but a dust heap of unrelated facts. The convergence of the testimony is remarkable and when we add to the chemical evidence that which is offered by physics the theory becomes overwhelmingly strong. And yet, from time to time, we are told that the theory has outlived its

[1] (Manchester Literary and Philosophical Society, Vol. 47, N. 11.)

usefulness and that it is now a hindrance rather than a help to science. When we say that matter as we know it, behaves as if it were made up of very small, discrete particles, we do not lose ourselves in metaphysics and we have a definite conception which can be applied to the correlation of evidence and the solution of problems. Objections count for nothing against it until something better is offered in its stead, a condition which the critics of the atomic theory have so far failed to fulfil.

"Up to a certain point we can easily dispense with the atomic theory, for we can start with the fact that every element has a definite combining number and then without any assumption as to the ultimate meaning of these constants, we can show that other constants are intimately connected with them. So far we can ignore the origin of the so-called atomic weight; but the moment we encounter the facts of isomerism or chemical structure, and of the partial substitution of one element by another, our troubles begin. The atomic theory connects all of these data together and gives the mind a simple reason for the relations which are observed. We cannot be satisfied with mere equations; our thoughts will seek for that which lies behind them."

The Ether of Mendeléeff

A suggestive "attempt at a chemical conception of universal ether" has been published lately by Mendeléeff. This is speculation, of course, but coming from the distinguished author of the Periodic System is well worthy of consideration. The chief reason for mentioning it here, however, is because it contains an interesting modification of his original Periodic Table of the Elements. Mendeléeff's propositions with regard to this ether, which permeates all bodies and fills all space, are as follows:

1. It must have weight, or mass, if it is matter.

2. Reasoning from its power of permeating all bodies and from its possible analogy to argon and its companions, he would think of ether as an inert gas incapable of combination.

3. He does not conceive of the other elements as formed from this and sees no simplification in a common origin of the elements. Unity of a higher order is given by the conception of ether as the final link in the chain of elements.

4. He forms a new group, therefore with ether = X and coronium = Y and then helium, argon, etc. This group is O. From considerations of molecular velocity he attempts to calculate the limits for the atomic weight of ether.

5. He believes that radioactivity indicates a material emanation and that the arrival and departure of ether atoms are accompanied by the disturbances which constitute waves of light. The chief cause of the sun's luminosity is its great mass, and the accumulation of ether due to its attraction. And thus ether is attracted by the great mass of the atom of uranium, thorium, radium, etc., explaining the radioactivity.

The table follows:

Periodic Table of Elements.

Series.	Group O.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
0	x								
1	y	H 1.008							
2	He 4	Li 7.03	Be 9.1	B 11	C 12	N 14.04	O 16	F 19	
3	Ne 19.9	Na 23.05	Mg 24.1	Al 27	Si 28.4	P 31	S 32.06	Cl 35.45	
4	Ar 38	K 39.1	Ca 40.1	Sc 44.1	Ti 48.1	V 51.4	Cr 52.1	Mn 55	Fe Co Ni (Cu) 55.9 59 59
5		Cu 63.6	Zn 65.4	Ga 70	Ge 72.3	As 75	Se 79	Br 79.9	
6	Kr 81.8	Rb 85	Sr 87.6	Y 89	Zr 90.6	Nb 94	Mo 96	..	Ru Rh Pd(Ag) 101.7 103 106.5
7		Ag 107.9	Cd 112.4	In 114	Sn 119	Sb 120	Te 127	I 127	
8	Xe 128	Cs 132.9	Ba 137.4	La 139	Ce 140	..	..	..	.. .. .. (..)
9		..	..	..	..	..	..	..	
10	..	..	..	Yb 173	..	Ta 183	W 184	..	Os Ir Pt (Au) 191 193 194.9
11		Au 197.2	Hg 200	Tl 204.1	Pb 206.9	Bi 208	..	..	
12	..	..	Rd 224	..	Th 232	..	U 239		

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