

An inaugural dissertation on a natural system of chemical classification : submitted to the public examination of the trustees and of the faculty of medicine of the College of Physicians and Surgeons in the city of New York, under the authority of the regents of the University of the State of New York, Alexander H. Stevens, M.D., president of the college and of the board of trustees for the degree of doctor of medicine, on the 6th day of February, 1845. / By Oliver Wolcott Gibbs, A.M. of the city of New York.

Contributors

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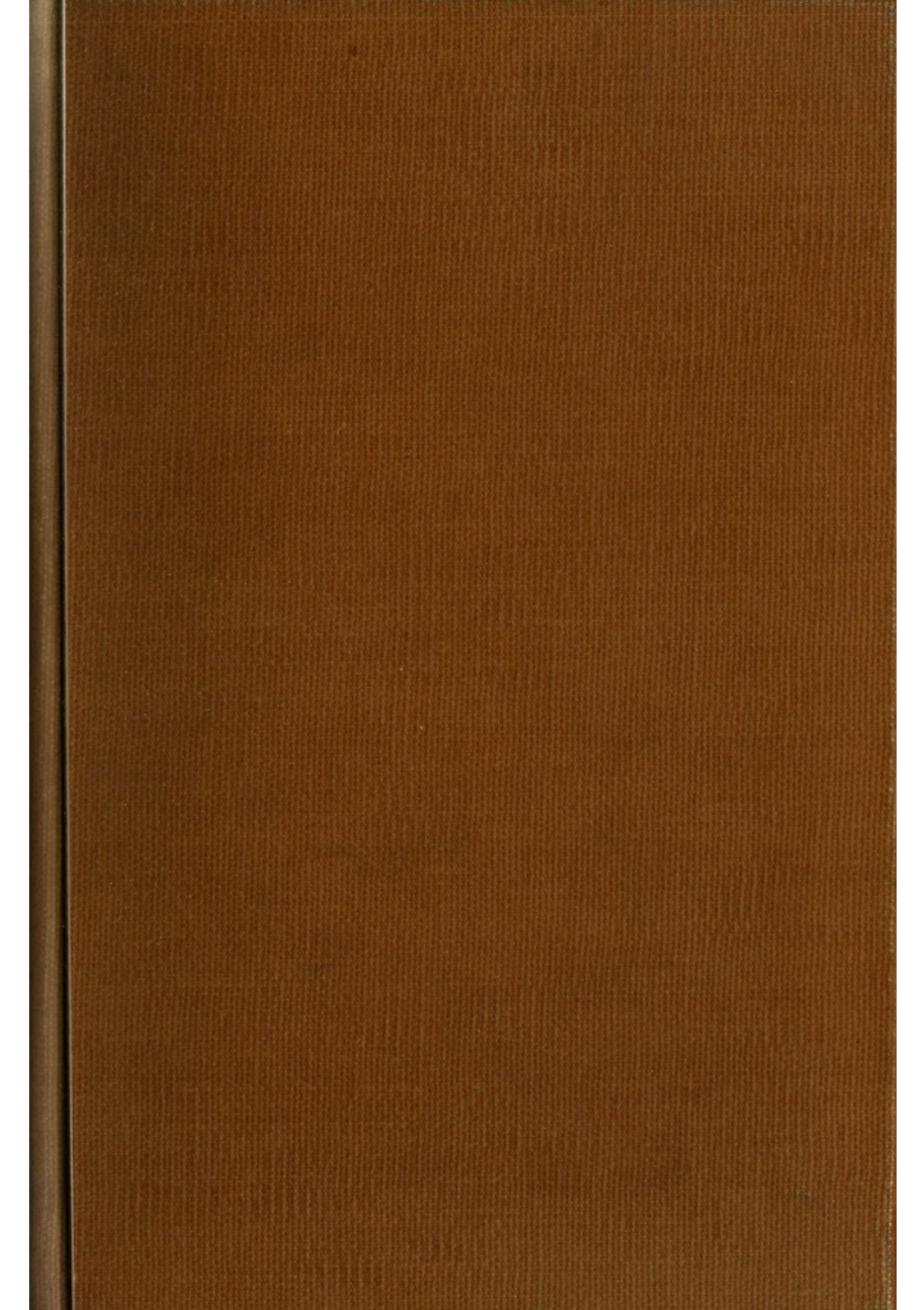
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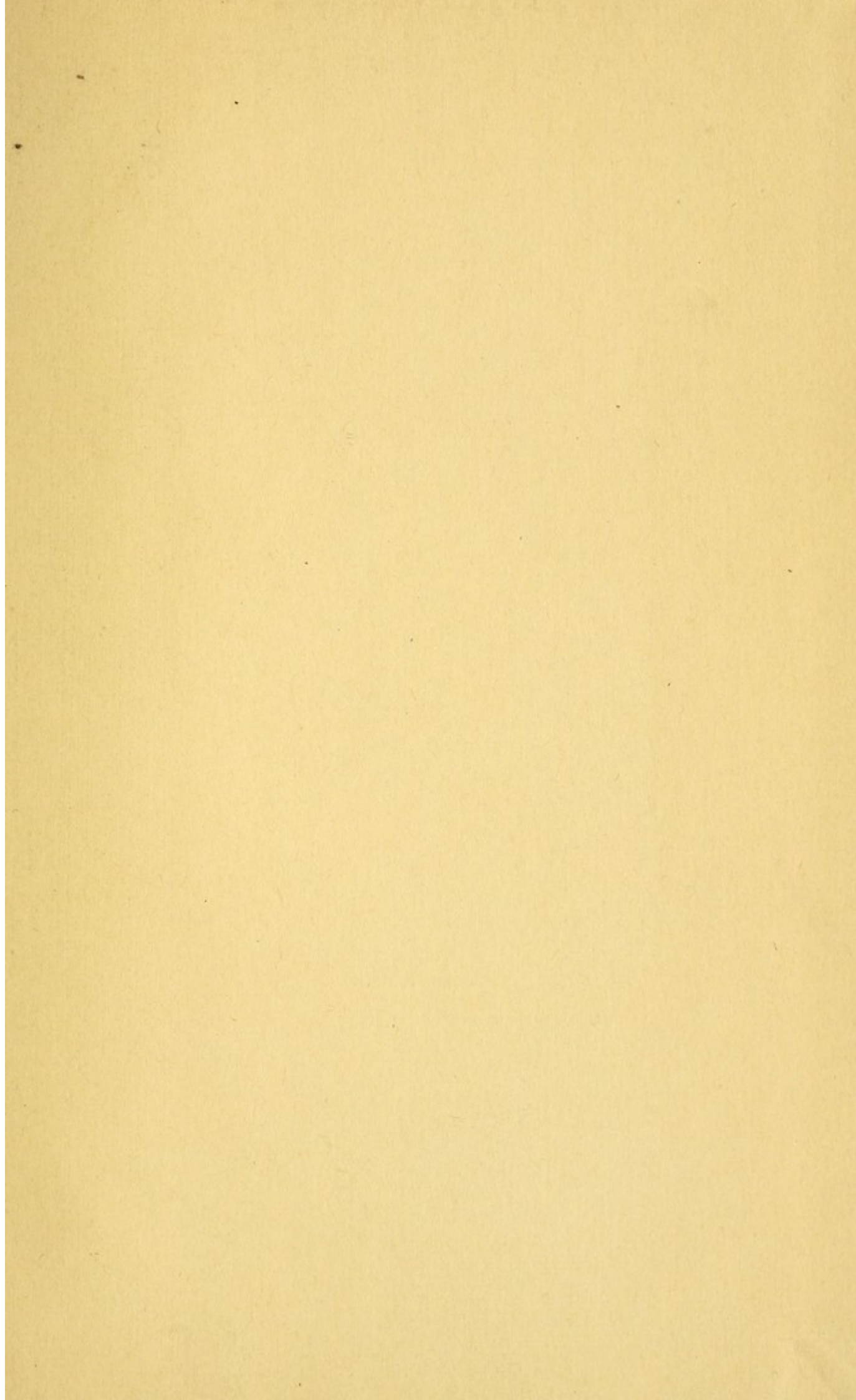


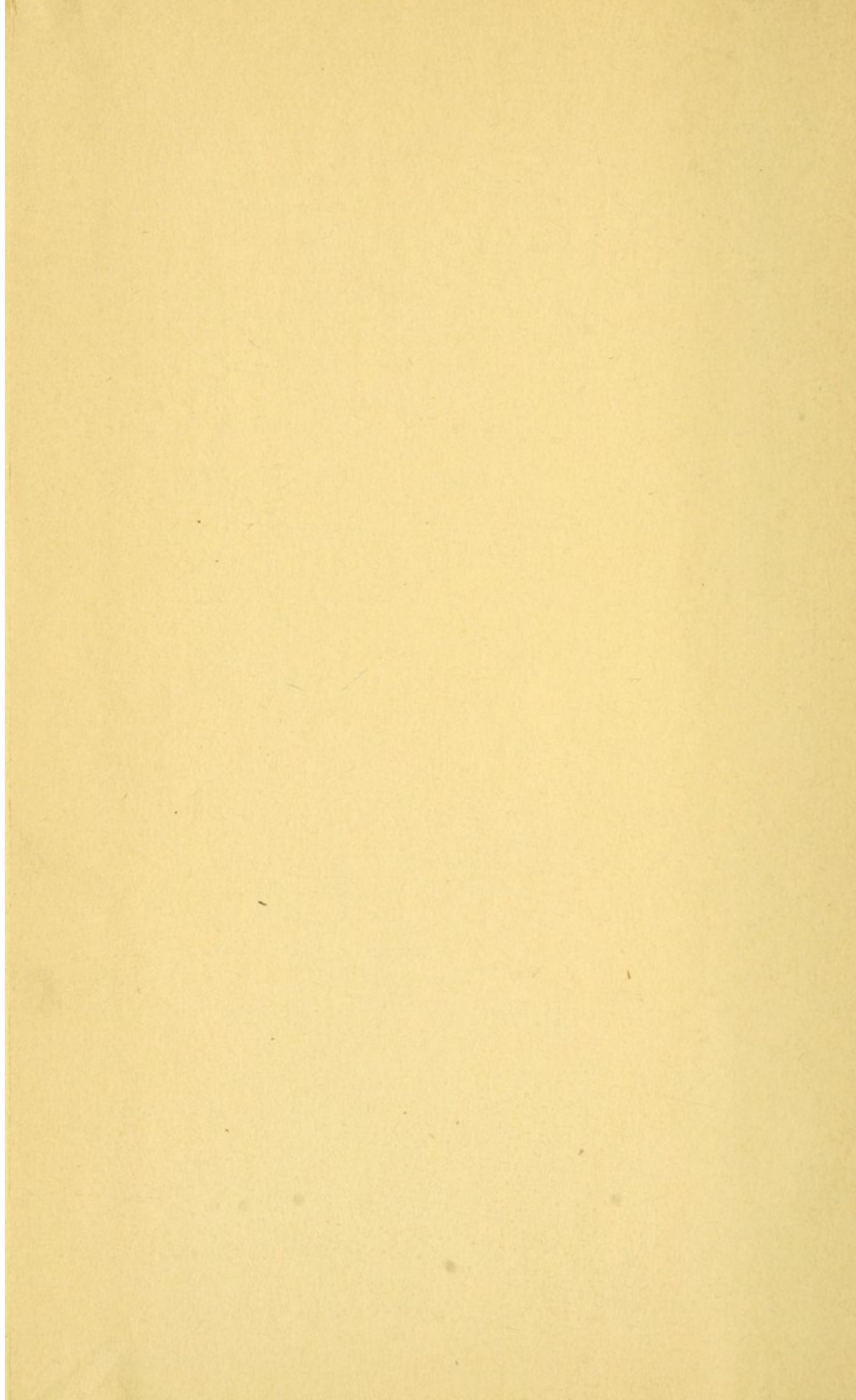
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AN
INAUGURAL DISSERTATION
ON
CHEMICAL CLASSIFICATION

BY
OLIVER WOLCOTT GIBBS, A.M.

AN
INAUGURAL DISSERTATION

ON A
NATURAL SYSTEM OF CHEMICAL CLASSIFICATION,

SUBMITTED TO THE PUBLIC EXAMINATION OF THE
TRUSTEES AND OF THE FACULTY OF MEDICINE
OF THE COLLEGE OF PHYSICIANS AND SURGEONS

IN THE CITY OF NEW YORK,

Under the authority of the Regents of the University of the State of New York,

ALEXANDER H. STEVENS, M.D.,
PRESIDENT OF THE COLLEGE AND OF THE BOARD OF TRUSTEES,
FOR THE DEGREE OF DOCTOR OF MEDICINE,

On the 6th day of February, 1845.

By OLIVER WOLCOTT GIBBS, A.M.
OF THE CITY OF NEW YORK.

PRINCETON, N. J.:
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1845

INTRODUCTION

TO

JOHN TORREY, M.D.

PROFESSOR OF CHEMISTRY AND BOTANY

IN THE COLLEGE OF PHYSICIANS AND SURGEONS,

This Dissertation is Respectfully Inscribed.

TO
JOHN TORREY, M.D.
Natura non facit saltum.

Linnaeus.

PROFESSOR OF CHEMISTRY AND BOTANY

IN THE COLLEGE OF PHYSICIANS AND SURGEONS

The Librarian is especially invited

INTRODUCTION.

The researches of chemists have resolved all known forms of matter into fifty-six separate and distinct species, which, having thus far resisted every attempt at further decomposition are termed elements, and must in the present state of our knowledge be regarded as simple substances. These Elements united in various proportions and with various degrees of energy, constituted in the beginning the entire mass of the Earth, and presented an Inorganic Nature, made up of vast bodies of gaseous and liquid matter, as well as of many successive series of rock, and of innumerable minerals, amorphous, or bounded by harmonious and symmetrically disposed planes, and constituting those regular figures which we term crystals. At a later period in the genesis of Nature, the mysterious power of Life was called into existence, and beginning perchance with the first cell-germ of the first lichen, spread at length over the whole Earth. Then innumerable new Forms came into being, and every plant, itself built up particle by particle and cell by cell of inorganic matter, became a laboratory wherein chemical decompositions and recompositions were perpetually going on through every step of growth, maturity and decay. At a still later period Life, gathering as it were new energy with the lapse of time, passed from the highest form of vegetable to the lowest form of animal organizations, and thence upward in the scale of being through every varying type and form, till it found in the structure of man the limit beyond which it was not destined to pass. The new and more complex organisms thus created, formed out

of the same elements new and more complex chemical products, adapted to their growth, their structure and their wants. The animal organism found in that of the plant, nearly all the materials necessary for its own sustenance : of some of these it changed the form without altering the chemical composition, while of others again it moulded the composition as well as the form anew. And when at length Life ceased longer to exert over each individual its plastic force, the elements obeying their mutual affinities formed new and simpler products, again to be brought under the sway of the vital force, and thus destined to pass through countless cycles of change, and to appear in the development and decay of myriads of organized forms. Could an atom of Carbon or of Hydrogen but speak to us what a history might it not unfold! Through every change however of the mineral, the plant, and the animal, the one universal law of Chemical combination—the law of definite proportions—has from the beginning of things, held good. Thus then we are led to recognize two great departments of Chemical Science, the Chemistry of Unorganized and the Chemistry of Organized bodies. The former embraces all those combinations which take place under the operation of purely chemical forces, whether in the laboratory of nature or under circumstances determined by the will of man. The latter comprehends all the products of the action of the vital force upon inorganic matter, whether this action be immediate as in plants or mediate as in animals, together with those bodies which result from the former by the action of chemical reagents. It is with the first of these departments that we have at present to deal. Between the fifty-six elements into which, as already stated, all known forms of matter have been resolved, there exist numerous remarkable analogies, which separate them first into subordinate natural families or groups, and then by general though not indistinct resemblances, unite them into one indissoluble chain, each link of which differs rather in degree than in kind from its fellow on either side ; so that the whole illustrates in unorganized nature, the truth of

the maxim of Linnæus—*Natura non facit saltum*, nature makes no leaps. And this then we assume as the fundamental idea and central point of our Essay, namely, that this law of grades which Linnæus announced for the organized kingdom alone, *is an universal law*, and prevails as well among lifeless atoms as among living beings, and in the simplest crystals as well as in the innumerable complex forms in which *Life* outwardly manifests itself. The forms of nature are many, but Nature herself is one. We propose then in the following pages to trace these analogies as they exist between those forms of matter which come within the range of Inorganic Chemistry, whether these be simple or compound, and to point out the most remarkable groups which such analogies constitute. The time and the occasion will not permit us to do more, though we would gladly extend our survey to the fertile and as yet but little tilled field of Organic Chemistry. Moreover, the classification of organic products must obviously depend upon a prior classification of the elements themselves, and upon an accurate knowledge of the nature and characters of those compounds which are united in virtue of chemical forces alone. By a chemical compound we shall of course understand any substance whose constituents are united in obedience to the laws of definite proportions, and we shall generally speaking divide compounds into binary, ternary, quaternary, &c., according to the number of their ultimate or of their proximate constituents. We may for the sake of convenience consider the subject under three heads:

1st. The analogies between simple substances and their division into groups.

2d. The analogies between compounds and their division into groups.

3d. The analogies between simple and compound bodies.

Before taking up the special consideration of the several groups, it will be well to dwell for a time in a general and concise manner upon some of the more important points in

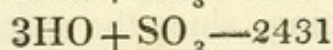
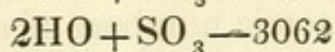
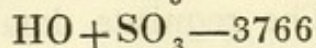
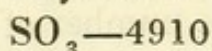
which the analogies about to be pointed out may subsist, and first then of the equivalent weights or combining masses.

1. The equivalents of a number of the elements appear to be connected together by simple numerical relations. The list of such instances of Isomerism originally given by Dumas, has since been considerably extended by Dr. Kane, and future researches, by correcting several of the equivalents at present received, will probably exhibit other cases of coincidence in this particular. Even now as we shall presently show, we may without straining our figures, add several to the list of instances enumerated by the last mentioned chemists. The bodies between which such isomerisms exist, for the most part resemble each other strongly in their chemical properties and general relations, notwithstanding the assertion of Dr. Kane that "in no case are their properties more different." The equivalent numbers of very many compounds, however, exhibit similar coincidences, without, at the same time, accompanying any analogies in composition or in chemical character. Such instances must of course be regarded as accidental, and must not be suffered in any degree to influence our systems of arrangement and classification. We arrive then necessarily at the conclusion that the chemical properties and relations of bodies do not depend upon their equivalent weights alone, but that in addition there are other and specific forces or properties which are inseparably connected with the constitution of each, and which bestow upon each its distinctive chemical character.

2. Admitting that the specific gravities of bodies represent the relative weights of equal bulks, it follows that if we divide the specific gravities by the atomic weights or equivalent numbers, we obtain the relative numbers of equivalents which different substances contain under the same bulk or volume. The numbers thus obtained have been termed by the German chemist by whom they were first observed, the Atomic Numbers, and appear to be deserving of more attention than they have as yet received. The atomic numbers of the elements

appear to be connected together in many instances by simple ratios, and the simple substances constituting a natural group, have usually the same number of equivalents contained under the same volume. The requisite data for instituting a comparison between the atomic numbers of compound bodies are for the most part wanting, since the specific gravities of very few of these last have been accurately determined. It is very much to be regretted, that this should be the case, since the greater the number of equivalents which a given compound contains under a given volume, the greater must be the energy with which its constituents are united and vice versâ, so that we are thus apparently furnished with an accurate method of determining Degrees of Affinity. To illustrate this by an example, let us take the case of Hydrate of Potassa and of monobasic sulphate of water. In a unit of volume the first of these bodies contains 3032, the last 3766, equivalents. The formula of the hydrate of Potassa is $KO + HO$, that of the sulphate of water $SO_3 + HO$. Consequently the affinity of water for sulphuric acid is greater than the affinity of water for potassa, in the proportion of 3766 to 3032, or the ratio of its affinity, for the two substances may be expressed by the fraction 1.2420. In like manner we find that the affinity of sulphuric acid for water is greater than its affinity for potassa, in the proportion of 3766 to 2745, so that if the principle which we have laid down be correct, there must be something more than a mere play of affinities exerted in the decomposition of sulphate water, $SO_3 + HO$, by hydrate of potassa, $KO + HO$. As a general rule, the greater the number of constituents which any substance contains, the less is its atomic number, and it is certain that a compound of two or more other compounds, manifests for the most part affinities less energetic than those of either of its constituents, and that in general the degree of neutrality is directly proportioned to the complexity of the composition. We shall endeavour to illustrate this position more fully hereafter, when treating of the several groups. It will be sufficient for the present to state the formula and the

atomic numbers of three definite sulphates of water, and of anhydrous sulphuric acid; they are as follows:



No connection has as yet been traced between the atomic numbers of a compound and those of its constituents. A connection however of some kind or other doubtless exists, and its discovery would be of the highest interest in a theoretic point of view.

3. Intimately connected with the atomic numbers, are the Combining Volumes, or the relative bulks of the equivalents in the gaseous state. If we consider the space occupied by an equivalent of Oxygen as unity, then an equivalent of Chlorine, of Iodine, of Bromine, of Hydrogen, and of a number of other bodies both simple and compound, occupies a space exactly twice as great. The equivalent of sulphur on the other hand, occupies, in the state of gas, but one-third the space which is filled by an equivalent of oxygen, of selenium, and of tellurium. It follows therefore that in *one* unit of space, there may exist 3 equivalents of sulphur, $\frac{1}{2}$ an equivalent of chlorine or of hydrogen, or one equivalent of oxygen, selenium or tellurium. To adopt for a moment the language of the atomic theory, the atom of chlorine in the gaseous state is twice as large as the atom of oxygen, the atom of sulphur but one-third as large, and so on for all other bodies simple or compound. The atomic volumes of all bodies then, while in the gaseous state, are connected by simple numerical ratios, and this fact is one of the deepest interest and importance. Of the 56 elements which are known to chemists, but a small proportion have been obtained or are found in the gaseous state. The combining volumes of a great number cannot therefore be experimentally determined, though in many cases they have been deduced *a priori* from clear and distinct analogies. The identity of two or more substances in this particular,

does not necessarily involve a similarity in general chemical properties and relations as will hereafter be shown.

4. By a process exactly the reverse of that employed in obtaining the Atomic Numbers, namely, by dividing the equivalent weights by the specific gravities, Dr. Kopp has obtained a series of numbers which he regards as expressing the atomic volumes of bodies; or in other words the relative volumes of their atoms; and he considers that his researches justify the conclusion that isomorphous bodies have the same atomic volume. The apparent deviations from this law exhibited by many isomorphous bodies, he regards as arising from the fact that substances are not *absolutely* isomorphous but only approximately so, and a glance at the numbers which he brings forward in support of his opinion, will abundantly justify the necessity of admitting this or some similar explanation.

5. Almost every unorganized body may be obtained in a crystalline state, and may consequently be arranged under some one crystallographic system, and have its interfacial and interaxial angles determined with a greater or less degree of accuracy. If now we institute a comparison between the crystalline forms of different substances simple or compound, we find that between those which are connected together by strong chemical analogies, there exists also certain definite relations of form, in many instances approximating toward identity. A natural family or group has in general the same crystalline as well as the same chemical types. Identity of crystalline form however by no means necessarily implies analogy in chemical constitution, since a substance composed of a great number of molecules of different kinds may crystallize in the same form as an element, and since on the other hand two elements may appear in crystallographic systems which have no connexion with each other. In fine, so numerous are the instances of agreement in chemical constitution and relations without a corresponding analogy of form, and again of a coincidence in crystalline form without a corresponding agree-

ment in chemical relations, that while similarity of form must ever be regarded as a strong reason for classifying together bodies which are otherwise analogous, yet the want of such a similarity will never of itself justify the separation of substances which agree in their general chemical relations. It is the too implicit reliance upon analogy of form which renders the classification proposed by Graham imperfect, and which has led him to associate together substances which differ widely in their chemical relations, and to separate others between which there exists in these respects the strongest resemblance. Certain bodies are met with crystallized in two different forms and isomorphous with two distinct classes or groups of other substances. Such bodies are said to be dimorphous, and serve to connect several groups together at once. The relation of dimorphism is subject to the same restrictions as that of isomorphism and must not be too strongly relied upon in classifying and arranging substances in natural families. No connection has yet been traced between the crystalline form of a compound and the crystalline forms of its constituents. The problem is one of the finest which offers itself to the enquiring mind, in the whole range of physical science, but sufficient data to form the basis of the solution are yet wanting. The chemical and physical history of no compound can be considered complete without an accurate and scrupulous determination of its crystalline form, and the negligence of chemists with regard to this most important particular cannot be too strongly reprobated. We shall hereafter point out a few instances in which a direct relation subsists between the forms of a compound and the forms of its elements. It may not be improper to note in this place the fact that as a *general* rule, the simpler the constitution of a body, the simpler also is its crystalline form and vice versa.

6. The relations of bodies to heat, though not sufficient in themselves to furnish grounds for associating them in groups are yet of very great interest and importance. The researches of Regnault and of Newmann and Aavgadro, have recently

afforded strong confirmation of the accuracy of Dulong and Petit's law, that the specific heats of equivalent weights of simple substances are equal. The few cases which appear to be exceptions to this law may easily be reconciled with it, not by an arbitrary subdivision of the atomic weights, but by a different enunciation of the law itself. Thus if we state that "the specific heats of the elements are either the same or are connected with each other by simple multiples," we obtain a clear and satisfactory explanation of the discrepancies which have thrown so much doubt upon the existence of any definite law whatever, and which have led to so many alterations of the equivalents and to so many improbable hypotheses. Between the specific heats of compound bodies there exist, also, similar relations, though they have not as yet been very fully studied. No connexion has been detected between the fusing or boiling points of different substances whether simple or compound and their chemical constitution or relations; though Gerhardt has recently succeeded in deducing an empirical formula, by which, having given the constitution and the boiling point of one liquid hydrocarbon and the constitution of a second, he is able to determine the boiling point of this last, by calculation alone. No connexion appears to subsist between the fusing or boiling point of any substance, and the number of equivalents which it contains in the unit of space. The quantity of heat which is developed during the act of chemical combination appears always to be definite, and depends upon the nature and composition of the substances uniting. The subject however has not yet been sufficiently investigated to admit of the deduction of definite laws. The same remark may be made with regard to the latent heats of all substances whatever. We are as yet very imperfectly acquainted with the subject. Neither the conducting powers nor the expansibilities of bodies appear to be connected with their chemical constitution.

7. Upon the consideration of the electrical relations we do not propose in this place to enter. The subject is as yet too

little understood to admit of anything more than a general application of these relations to the purpose of classification. We shall point out in speaking of the several groups, the electrical conditions of each, agreeably to the theory of Faraday and Berzelius, though we do not propose to adopt this as the basis of classification, as is now very commonly done.

8. The influence which the chemical constitution of a body exerts upon the transmission, reflection, absorption or polarization of Light, has hitherto excited very little attention. No connexion has been traced between the refractive power of a compound and the refractive powers of its constituents, and very few data exist with which to institute a comparison. Possibly the action of bodies upon Light may be connected with their Atomic Numbers, but the whole subject is involved in the deepest obscurity and presents a noble field for experimental research.

9. It remains to consider in a brief and general manner, the purely chemical relations of bodies to each other, that is to say, the relations of constitution, of acidity and basidity, of molecular types and of general character and properties. The molecular type of any substance is of the utmost importance in the determination of the group to which it belongs. As the elements are to the best of our knowledge identical in this particular, we are obliged, in order to investigate their chemical relations, to examine the molecular structure of the compounds which they form with one another, and from these to deduce the general character of each. We find then that a natural group of Elements, by entering into combination with other elements, forms a series of compounds whose molecular structures are precisely similar to one another, and which may be transformed the one into the other by a simple change in the chemical symbols which constitute the formulæ. In like manner a natural group of compound bodies is composed of substances which are exactly parallel to one another, both in composition and in the arrangement of their constituents. Bodies which are similarly constituted exhibit for the most part very

similar relations toward other bodies, and conversely we are often able to decide upon the constitution of a body by the analogy which exists between its properties and those of another substance whose composition is already known. The relations of acidity and basidity depend strictly upon molecular type, and are purely relative, a substance which in one connexion is an acid, is in another a base, and in another again, neutral. The neutrality of any compound is for the most part in proportion to the number of secondary compounds of which it is composed, neutrality being here used in the sense of incapacity to enter still further into combination. Certain of the elements generate by uniting with other elements compounds, which are either acids or bases; others again generate new substances which are eminently neutral and incapable of forming new compounds with one another. The union of certain bodies is accompanied with the development of light and heat, with others again no such phenomena are visible during the act of combination. Many substances are capable of uniting directly with each other, when brought together in a free state and at ordinary temperatures, the affinities of others again must be modified by heat, light or electricity, before they can be made to combine. Finally the three states in which bodies present themselves, as solids, liquids or gases, *appear* to depend upon their relations to heat alone, and to have no definite relations to their chemical constitution or properties.

We have thus taken a brief survey of some of the most important points in which the chemical analogies of bodies subsist, and we now proceed to the consideration of the several groups which are constituted by the elementary substances.

GROUP I.

The first group comprises eight elements. Oxygen, Sulphur, Selenium, Tellurium, Chlorine, Bromine, Fluorine. Between these eight elements, though widely different in the

common physical properties of matter there exist the most intimate chemical relations, so that as a whole the group constituted by them is more strongly marked than any other. These relations are as follows :

1. A body belonging to any other group commonly unites with a member of this, with that evolution of light and heat which chemists term combustion.

2. The affinities of the members of this family are more energetic and are exerted through a wider range than those of any other family. And this is proved by the number and variety of the compounds which they form with other substances ; by their combining, as a general rule, at much lower temperatures than other substances, and by their capacity of entering into direct combination, while in a free state.

3. The eight elements composing this group are capable of replacing each other in a compound of given molecular type without altering that type, and without altering, otherwise than in degree, the chemical relations of the primitive whence the new substances are by substitution derived. The new substances will be acids, bases or neutral, according as that from which they are supposed to be derived was acid, base, or neutral.

4. The existence of any particular compound or compounds of a substance not belonging to group 1st, with any member of this group, is an *à priori* evidence, that there may also exist similar compounds of the other members of group 1st with the substance in question. Thus the different groups of chlorides, oxides, sulphides, &c. are exactly parallel to one another in composition, and as already remarked, (3) differ in their chemical relations only *in degree*.

5. A compound of one equivalent of a member of this family, with one equivalent of a radical simple or compound, performs in general the part of a base, though as already remarked one base may act the part of an acid toward another. As the number of equivalents of the substance belonging to group 1st, increases, the acidity of the compound also in-

creases. A binoxide or bichloride is feebly basic toward powerful oxacids or chloracids, and feebly acid toward powerful oxy-bases or chlorobases. A teroxide or terchloride is in almost all cases a powerful acid, and a pentoxide or pentachloride still more so.

6. Substitutions of one member of group first for another may be either complete or partial. Thus chlorine may either replace 3 equivalents of oxygen in a teroxide, or only one. We meet for example with such compounds as SO_2Cl , CrO_2Cl , $\text{Fe}_2\text{O}_2\text{Cl}$, COCl , and many others of a similar constitution. Such compounds will of course be most conveniently classed with the substance from which they are or may be considered to be derived.

7. Between the equivalent weights of several members of this group remarkable relations are found to subsist. Thus, Oxygen, Sulphur, and Tellurium appear to be isomeric, their equivalents being to each other as 8, 16 and 64, very nearly, or as 1, 2 and 3. Selenium on the other hand, which very closely resembles Sulphur in its chemical relations, is entirely unconnected with it in this particular, but its equivalent is very nearly half that of Bromine. $\text{Se} = 39.63 = \frac{78.39}{2} = 39.19 = \frac{1}{2} \text{Br}$.

Chlorine, Iodine and Bromine do not appear to be connected by any definite relations between their atomic weights, and future researches may show that there is no real isomerism between Selenium and Bromine.*

8. The combining volumes of Oxygen, Selenium and Tellurium are equal to each other and are represented by unity. The combining volume of Sulphur is 3 times, and that of Chlorine, Iodine, Bromine and Fluorine twice, as great as that of Oxygen. Hence either the atom of Chlorine is twice as large as the atom of Oxygen or else Oxygen contains in the same space twice as many particles or atoms as Chlorine does. This last is perhaps the more probable opinion of the two.

* According to Dumas, the equivalent of Selenium is 40, which makes it isomeric with Oxygen: $8 \times 5 = 40$.

9. The atomic numbers of Chlorine, Iodine and Bromine are the same, that is to say, one unit of space contains an equal number of equivalents of each of these substances. The numbers themselves are, Chlorine 383, Bromine 380, Iodine 392, the mean of which is 385, which may therefore be considered as representing the true atomic number of the 3 substances in question. The atomic numbers of Sulphur and Selenium are apparently unconnected; they are, of Sulphur 125, of Selenium 109. As Oxygen has not been obtained in a solid, and Fluorine in an isolated state, their atomic numbers cannot of course be determined. Tellurium is connected neither with Chlorine and Bromine, nor with Sulphur or Selenium by any very certain relations of atomic numbers. It contains in one unit of space 978 equivalents, which is very nearly 9 times as many as are contained within the same volume of Selenium. $109 \times 9 = 981 = 978 + 3$.

10. As a general rule an oxide appears to contain under the same bulk a greater number of equivalents than a corresponding sulphide, and a sulphide a greater number than a corresponding chloride. Such at least is the conclusion which the writer has drawn from his own calculations which are all which he has had to rely upon. The following tables will exhibit this to a limited extent. (Note. The specific gravity of water is here taken as 1000.)

Pb=11030, PbO=8504, PbS=6336, PbCl=4080, Aq=9640, AqO=6139, AqCl=3894.

Hg=13210, HgO=10119, HgCl=3754, Hg²O₂=8097, Hg 2Cl=2932.

Perhaps a more extended induction may overthrow the opinion which we have advanced in regard to the atomic numbers of oxides, sulphides and chlorides. But if on the contrary more accurate and extensive observation shall demonstrate its correctness, it will then as it seems to us, afford an explanation of many facts in the history of these bodies which are at present involved in obscurity. For does not a very great degree of condensation imply a very energetic at-

traction? and does not a lesser degree of condensation imply a weaker attraction? The subject is at any rate worthy of a most thorough and careful study.

11. Between the atomic volumes of certain members of this group there also exist remarkable relations. Thus by dividing the atomic weights of Chlorine, Iodine and Bromine by their respective specific gravities we obtain as quotients, 25, 25, 26, and we therefore conclude that the atomic volume or the bulk of the equivalent is the same for each of these bodies. Thus not only are there as we have already shown (9) the same number of equivalents in the same bulk of each of these bodies, but the bulk or volume of each of these equivalents is also the same. And this last is by no means a necessary consequence, as might at first appear, of the first. For as it is clear that matter, whether it consist of atoms or not, is not continuous through space, so it must be evident that one unit of space, one cubic inch for example, may contain either very different numbers of equal-sized atoms or the same number of atoms differing in size, or again, different numbers of different atoms, provided only that these atoms are unequally distant from each other in the three cases which we have supposed. The volume of the atom of Tellurium is to the volume of the atom of Sulphur or Selenium as 10 to 8 or as 5 to 4, and to the volume of the atom of Chlorine, Iodine or Bromine as 10 to 25 or 2 to 5. The atomic volumes of Oxygen and Fluorine as well as their atomic numbers are of course unknown.

12. Of the 8 elements which compose group 1st, Sulphur and Selenium are isomorphous. Chlorine, Bromine and Iodine are also isomorphous, and possess besides the same atomic volume and the same atomic number. The compounds of Fluorine are also uniformly isomorphous with those of Chlorine, Iodine and Bromine, and we have therefore strong reasons for regarding Fluorine as itself isomorphous with Chlorine, Iodine and Bromine. Tellurium is not connected with the other members of Group 1st by isomorphism, unless indeed it should prove like Sulphur to be dimorphous. Finally,

the crystalline forms of the sulphur salts have not been sufficiently studied to enable us to form any idea of the crystalline form of Oxygen, by instituting a comparison between the two classes of salts, which Sulphur and Oxygen are respectively capable of generating. We may notice in this connexion a fact which does not seem to have attracted the attention of chemists. The crystals of many anhydrous protochlorides, protiodides, protobromides, and protofluorides belong to the regular system, being for the most part either cubes or regular octahedra. Furthermore, the crystals of many double protochlorides, double protiodides, &c. are also met with in the regular system. In order not to leave this assertion without proof or illustration, we will cite the formulæ of a few compounds together with their crystalline forms.

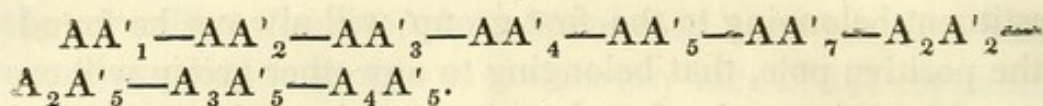
(KCl, NaCl, AqCl, KI, KB_2 , CaF, NaF, NaB_2), cubes. (AqCl + KCl), (AqCl + NaCl, AqCl + HCl), cubes. Many protochlorides and protobromides crystallize with water, and their form is thus rendered more complex. Other relations of form and composition will be pointed out when treating of other groups.

13. The specific heats of certain of the elements connected with this group appear to bear a definite relation to each other. Thus the specific heat of an atom of Sulphur being considered as unity, that of an atom or equivalent of Tellurium is represented by 2, or is twice as great, that of Iodine again is 4 times as great as that of Sulphur and twice as great as that of Tellurium. The specific heats of equivalent weights of the other members of group 1st have not yet been accurately determined.

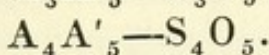
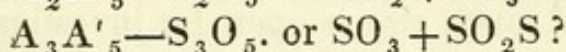
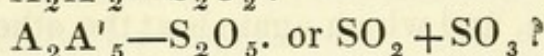
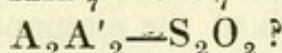
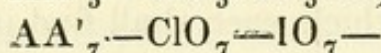
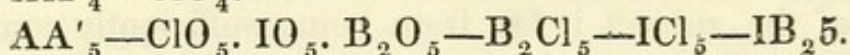
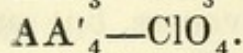
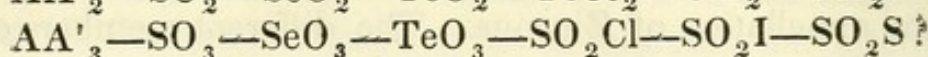
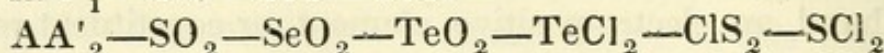
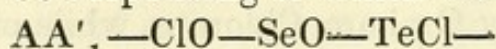
14. The elements composing this group are more highly electro-negative than any other substances which we are acquainted with. In the electro-chemical theory they constitute, par excellence, the electro-negative group, and they are separated from the other groups in this respect by a wide interval. If a compound of an element belonging to this family with one belonging to any other, be submitted to electrolysis, the

constituent belonging to the first group will always be found at the positive pole, that belonging to any other group will on the contrary always be found at the negative pole. An electro-negative element is termed by Graham, Chlorous, while on the other hand an electro-positive element or constituent receives the appellation of Zincous. The different members of the group differ in the degree of electro-negativeness, but our knowledge of the subject is far from being sufficiently complete to enable us to form a scale in which each shall find its proper place, or even to say positively which of the elements is most highly electro-negative, and which again is at the other end of the scale. This and much else is open for investigation.

15. It remains to consider the different members of this group in their relations with each other. With the exception of Fluorine and of course Oxygen, they all agree in forming with Oxygen, compounds which for the most part are powerfully acid. The types of these compounds are not in the present state of our knowledge perfectly parallel. Sulphur forms with Oxygen 6 distinct acids, of which but one, namely, hypsulphuric acid has its analogue among the Oxygen compounds of Chlorine, Iodine and Bromine, while two, namely, sulphurous and sulphuric acids, have analogues among the compounds of Selenium and Tellurium. Chlorine again forms 4 compounds with Oxygen, to which Iodine offers but two parallels, and Bromine but one. Finally, Selenium offers one compound, the protoxide, which agrees in composition with hypodelorous acid or protoxide of Chlorine. In order to exhibit at once the general types of the compounds of this group, we will assume the letter A to represent any member of the group in a general formula, accenting it thus A' or A'' when necessary to consider or represent more than one element at the same time and in the same formula. Adopting these symbols then we may construct general formulæ which will represent the types of all known combinations of the members of this group with one another, and these types we find to be as follows :



Corresponding to which we have



We have already alluded to the number and characters of the compounds which the members of this group form with those of other groups, and this portion of the subject will also meet with further consideration in speaking of the other groups, specially and individually.

The bodies which we have arranged together under this first class compose the first and fifth classes of Graham. They are collectively termed Basacigen by Dr. Hare, in reference to their property of forming both acids and bases by uniting with other substances. By the latter chemist also this group is again, in deference to the opinions of Berzelius, subdivided into two, the first termed Amphigen, comprising Oxygen, Sulphur, Selenium, Tellurium; the second termed Halogen, comprising Chlorine, Iodine, Bromine and Fluorine. As the term Amphigen has not come into very general use, it might be well to substitute it for the term Basacigen, which though very expressive in itself is not susceptible of etymological changes. Should it be thought worth while to subdivide the whole group into two sub-groups, then for the same reason that Chlorine, &c. are termed Halogen, Oxygen, Sulphur, &c. might be termed Alkaligen, as has indeed been proposed by some German chemists. Perhaps the best nomenclature after all would be the simplest, viz: to associate all the elements under the title of the Oxy-Chlorine Family.

GROUP II.

The second group comprises Nitrogen, Phosphorus, Arsenic and Antimony. The parallel between the chemical properties and relations of these four elements is for the most part very striking. If we assume the letter R as a general symbol for the whole group, while A represents, as before, any element belonging to group 1st, we shall find the following types for the compounds of the two groups. $RA-RA_2-RA_2-RA_4-RA_5$, corresponding to which we have

to $RA-NO-PO$

to $RA_2-NO_2-AsS_2-$

to $RA_3-NO_3-NS_3-PO_3-PS_3-PCl_3-PBr_3-PF_3-AsO_3-SbO_3-AsS_3-SbS_3-AsCl_3-SbCl_3 + \&c.$

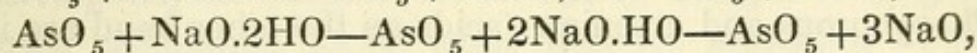
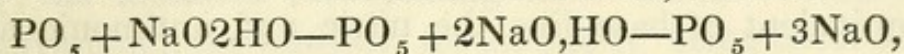
to $RA_4-NO_4-SbO_4-SbS_4-SbCl_4.$

to $RA_5-NO_5-PO_5-AsO_5-SbO_5 + \&c. \&c.$

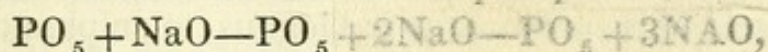
In addition to these, phosphorus forms a suboxide to which there is no analogue among the other elements of the 2d group. Besides the analogies of the compounds which the members of this group form with those of group 1st, there are also other and not less remarkable relations. Each member of group 2d forms with hydrogen a gaseous compound of the type RH_3 . These compounds are severally represented by the formulæ NH_3, PH_3, AsH_3, SbH_3 . The first and second of these unite with the halides of hydrogen to form definite compounds, strongly analogous to metallic halides and of the type $RH_3 + HA'$. The first again, ammonia, is capable also of uniting with the oxides, sulphides, &c. of hydrogen to form powerful oxybases and sulphobases, which moreover are isomorphous with similarly constituted oxides and sulphides of potassium. To these compounds, the phosphuret, arseniuret and antimoniuret of hydrogen offer no parallels. Again, ammonia and phosphuretted hydrogen are capable of forming a very numerous class of compounds by combining directly with oxides, chlorides, &c. as well as with very many classes of salts composed of acids and bases. Antimoniuretted and arseniuretted hydrogen appear to form no such com-

pounds. One equivalent of the hydrogen of ammonia may be replaced by an equivalent of metal forming a body of the type NH_2M , and presenting characters very analogous to those of a protoxide or protochloride. We do not know that either of the compounds of the other three members of this group with hydrogen are susceptible of a similar molecular replacement. Lastly, by means of a voltaic current, certain of the compounds of ammonia, those namely, with the halides of hydrogen, may be decomposed, the ammonia uniting with an equivalent more of hydrogen to form a compound metal which forms with the mercury which constitutes the negative pole of the battery, a true amalgam, while the halogen constituent is given off at the positive pole of the circuit. We are as yet ignorant whether the compounds of phosphuretted hydrogen with the halides of hydrogen are or are not capable of undergoing a similar decomposition, and whether or not there may be a compound of phosphorus and hydrogen exactly analogous to the hypothetical ammonium, and like it forming an amalgam with mercury. And it would be a most deeply interesting experiment, to submit to electrolysis in contact with mercury the compound of phosphuretted hydrogen and iodo-hydric or bromohydric acid, represented by the formula $\text{PH}_3 + \text{HI}$ or $\text{PH}_3 + \text{HBr}$, and to determine whether these compounds are not, like the iodide and bromide of ammonium, in all chemical relations, true iodides and bromides and not idohydrates and bromohydrates. It has been shown by Rose that a compound of phosphorus, hydrogen and chlorine, exactly analogous to sal-ammoniac, exists in combination with bichloride of titanium, forming a lemon-yellow substance, whose formula is $\text{PH}_4\text{Cl} + 3\text{TiCl}_2$. The combinations of the members of this group with hydrogen, illustrate the law of grades in a very striking manner, those chemical properties and relations which are most strongly marked in the nitrogen compounds, shade off as it were first into the phosphurets, then the arseniurets, and finally are lost, or at best very feebly exhibited in the antimonurets, of hydrogen. In the com-

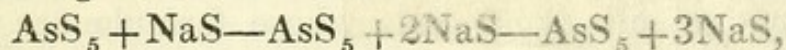
pounds of the members of this family with those of the first group, equally striking analogies are manifested. For example, the nitric and antimonie acids NO_5 and SbO_5 unite with but one equivalent of base, phosphoric acid PO_5 unites with one, two, or three, while arsenic acid again AsO_5 , unites with three equivalents of base alone. For the formulæ of the tribasic salts of the two last mentioned acids, we have



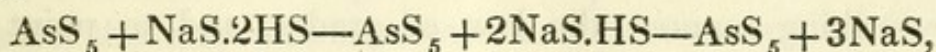
which formulæ it will be seen are mutually convertible, by the simple interchange of the symbols for phosphorus and arsenic. Though arsenic acid forms but one class of salts, yet the type of the three classes of salts formed by phosphoric acid is not lost with the compounds of arsenic, but distinctly manifests itself in the sulpharsenates. Thus we have the formulæ of the three classes of phosphates, viz: the monobasic, the bibasic and the tribasic phosphates, as follows:



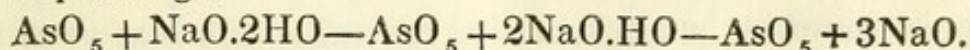
corresponding to which we have



formulæ which are mutually convertible, by the interchange of symbols for oxygen and sulphur. Here again the law of grades is beautifully exhibited. We are as yet unacquainted with any tribasic sulpharsenate, corresponding to the tribasic arsenates and phosphates whose formulæ are given above, and which contain both a stable and an unstable base. It is clear that should such compounds ever be formed, sulphides of hydrogen will take the place in the sulpharsenates of the oxide of hydrogen in the oxyarsenates, so that we should have

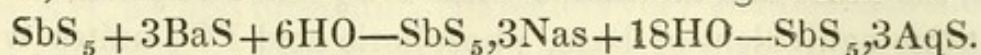


corresponding to



The salts formed by the sulphides of nitrogen and phosphorus have not yet been studied and are well worthy of attention. The nitric and antimonie acids as already observed

unite with but one equivalent of base; on the other hand however it appears certain that the sulphantimonic acid is tribasic, the formulæ of several of its salts being as follows:



which obviously correspond with the tribasic phosphates, arseniates and sulpharseniates. Still further, the nitrous and antimonious acids NO_3 and SbO_3 appear to unite with but one equivalent of base like the nitric and antimonic acids. Phosphorous and arsenious acids on the other hand are in all probability tribasic, all the known salts of the former acid being constituted upon the formula $\text{PO}_3 + 3\text{RO}$ while those of arsenious acid appear to come under the formulæ $\text{AsO}_3 + 3\text{RO}$, $\text{AsO}_3 + 2\text{RO}$, $\text{AsO}_3 + \text{RO}$, and thus to be monobasic and bibasic as well as tribasic. In like manner the formulæ of the sulpharseniates demonstrate an exact analogy between them and the arseniates, the formulæ of the two classes of salts being $\text{AsO}_3 + (1, 2, 3)\text{RO}$ and $\text{AsS}_3 + (1, 2, 3)\text{RS}$. Sulpharsenious acid appears closely analogous to sulphantimonious acid as the two form in combination with basic sulphides numerous native salts or minerals whose formulæ are precisely similar. The general formulæ of the sulphantimonites like those of the sulpharseniates may be expressed by $\text{SbS}_3 + (1, 2, 3)\text{RS}$, corresponding to which we have

Zinkenite $\text{SbS}_3 + \text{PbS}$ —Feather Ore $\text{SbS}_3 + 2\text{PbS}$ —Boulangerite $\text{SbS}_3 + 3\text{PS}$ —Ruby Silver $\text{SbS}_3 + 3\text{PbS}$.

We have dwelt upon sulphur salts of the members of this group at considerable length, both on account of their intrinsic interest, and because, though their formulæ are stated in many works on Chemistry, no deductions whatever appear to have been drawn from them. They appear to us to illustrate in a very striking manner the law of grades, and to point out many paths of research upon which at some future period we hope to enter.

Of the 4 elements which compose this group, two, viz: arsenic and antimony are isomorphous in their free or uncombined state. The salts of phosphoric and arsenic acids which

are similar in constitution correspond also in form. No certain isomorphism connects the compounds of hydrogen with this group, while on the other hand the isomorphism of antimony and arsenic with tellurium preserves a resemblance in this respect between groups first and second.

Notwithstanding the isomorphism of arsenic and antimony, the numbers representing their atomic volumes do not correspond, the number for antimony being according to our own calculation 19.22 while that for arsenic is 12.68. Hence there must be some exceptions to the law of Dr. Kopp. There is a similar disagreement between the atomic numbers of the two substances, the number for antimony being .0519 while that for arsenic is .0792.* Yet it seems to us that these apparent discrepancies rightly considered, will entirely disappear. Adopting for the sake of simplicity the atomic theory, we reason as follows: arsenic and antimony are isomorphous—the volume of the atom of arsenic is less than that of antimony in the proportion of 12.68 to 19.22, but in the same bulk a crystal of arsenic contains more atoms of arsenic than a crystal of antimony contains atoms of antimony, in the proportion of .0792 to .0519; if therefore we multiply, for each element, the volume of one atom by the number of atoms in a crystal of each, is it not perfectly clear that we obtain the volume or bulk of all the matter, arsenic or antimony, which each crystal contains? On submitting our reasoning to the rigid test of calculation we actually find that a crystal of antimony and an equal crystal of arsenic contain the same volume of matter, for $.0519 \times 19.22 = .997518$ and $.0792 \times 12.68 = 1.004256$ the difference being only .006738, a coincidence which must be regarded as very remarkable, when we consider the unavoidable errors in the determinations both of the specific gravities and the atomic weights. Still further, we have said that tellurium is isomorphous with arsenic and antimony; now the atomic volume of tellurium is .978 and

* The sp. gr. of water is here taken as unity and not as before 1000.

its atomic number 10.22, multiplying these two together we obtain 9.99516 which is almost identical with the numbers already obtained for antimony and arsenic! Thus we have

Arsenic = 1.004256 = unity very nearly.

Antimony = .997518 = “

Tellurium = .999516 = “

Mean = 1.000430 = “

We might perhaps apply to the numbers thus obtained, viz: by multiplying the atomic volumes by the atomic numbers, the term “crystalline volumes.” Yet it will be immediately obvious, from a consideration of the manner in which the atomic numbers and the atomic volumes are obtained, that their product must *always* be unity, since if W represent the atomic weight of any substance and S its specific gravity, we shall have for the atomic number $\frac{S}{W}$, and for the atomic vol-

ume $\frac{W}{S}$, now $\frac{S}{W} \times \frac{W}{S} = \frac{SW}{SW} = 1$. and since the same is true for all substances whatever, whether simple or compound, it follows that the crystalline volumes of all bodies are equal, that is to say, every substance whatever, no matter what may be its form or what its constitution, contains within a unit of volume, one cubic inch for instance, the same volume of *ponderable* matter. This may be stated otherwise as follows: “The volumes of the atoms of all substances are inversely proportional to the number of atoms which are contained under the same surface.” This law may be made of great use in the determination of the atomic weights of different substances. Its truth appears to us incontrovertible, if we admit the truth of the premises. The members of group 2d are connected with those of group 1st, as already observed by the isomorphism of tellurium with arsenic and antimony. In addition to this, however, there are other points of resemblance which are not unworthy of notice. Thus, the nitric, phosphoric, arsenic and antimonie acids are analogous in constitution to the iodic, chloric and bromic acids, while nitrous, ar-

senious, phosphorous and antimonious acids find parallels in sulphuric, selenic and telluric acids. Hypo-nitric and hypo-antimonic acids again are analogous in type to chlorous acid; NO_4 and SbO_4 to ClO_4 . Antimonious acid moreover resembles the iodic in mode of combination as well as in constitution, thus we have $\text{KO} + \text{SbO}_5$ and $\text{KO} + 2\text{SbO}_5$, corresponding to $\text{KO} + \text{IO}_5$ and $\text{KO} + 2\text{IO}_5$. Arsenic and antimony, the former especially, appear sometimes to replace sulphur in combination, and to act the part of basacigen bodies. Thus we have $\text{FeS}_2 + \text{FeAs} - \text{CoS}_2 + \text{CoAs} - \text{NiS}_2 + \text{NiAs} - \text{Co}_2\text{As}_3 - \text{FeAs} - \text{Ni}_2\text{As} - \text{Mn}_2\text{As} - \text{NiS}_2 + \text{NiSb} - \text{Ni}_2\text{Sb}$ which we may assimilate to $\text{FeS}_2 + \text{FeS}$ or $\text{Fe}_2\text{S}_3 - \text{CoS}_2 + \text{CoS}$ or $\text{Co}_2\text{S}_3 - \text{NiS}_2 + \text{NiS}$ or $\text{Ni}_2\text{S}_3 - \text{Mn}_2\text{S} - \text{Ni}_2\text{S}$, where arsenic and antimony appear to be substituted for an equivalent of sulphur in the metallic sesquisulphides.

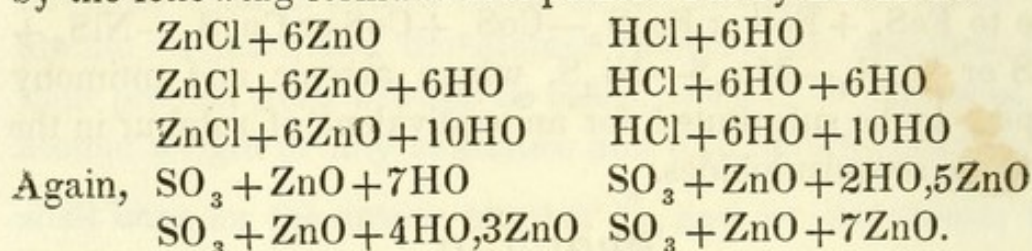
GROUP III.

The third group comprises also four elements. They are Hydrogen, Zinc, Cadmium and Magnesium, which collectively form an extremely well defined natural family. The types of the compounds of these elements with the members of the 1st or basacigen group are few and simple. If as usual A represents a member of group 1st, and R any element belonging to the group now under consideration, we may comprehend all the combinations of the members of the two groups under the general formulæ,

$\text{R}_2\text{A} - \text{RA} - \text{RA}_2$, corresponding to which we have $\text{Zn}_2\text{O} ?$
 $-\text{ZnO} - \text{ZnO}_2 - \text{HO} - \text{HS} - \text{HO}_2 - \text{HS}_2 - \text{CdO} - \text{MgO} - \text{ZnCl}$
 $-\text{HCl} - \text{CdCl} - \text{MgCl}$, &c. &c.

The three peramphides or rather deut-amphides of this family, viz: $\text{ZnO}_2 - \text{HO}_2 - \text{HS}_2$ are remarkable for the instability of their composition, and hence it is not very probable that we shall ever obtain higher oxides, sulphides, &c. All the proto-amphides of the members of this group are on the other hand remarkable for stability and form very powerful bases which enter into the composition of a great number and variety of salts. The similar salts of the protoxides of zinc,

cadmium and magnesium are isomorphous. Hydrogen is connected with the others by numerous and striking analogies, though it enters into the constitution of innumerable substances which find no parallels among the combinations of the other members of the group. Recently, indeed, it has been shown by Dr. Kane that hydrogen is to be regarded as a metal, differing from other metals simply in physical constitution, being at ordinary temperatures a gas, in the same manner and for the same reason that mercury is at ordinary temperatures a liquid. The analogies of hydrogen to zinc, are strikingly illustrated by the following formulæ first pointed out by Dr. Kane.

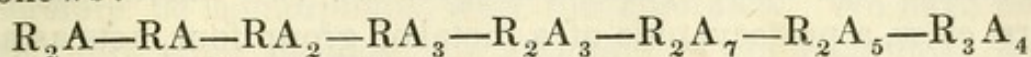


The equivalent weights of the members of this group are not connected by any simple multiples, in other words they are not isomeric. The atomic numbers of zinc and cadmium are very different, that of the former being 21430, that of the latter 15570. Their atomic volumes are consequently also different. All the members of the group are in a high degree electropositive; the replacement of an equivalent of hydrogen by an equivalent of zinc being the method universally employed to generate voltaic currents. This group is not connected with the second by any definite links, in the present state of our knowledge, and its relations to group 1st are dependant chiefly upon its intimate connexion with the next family, with which indeed it is associated both by Graham and by Kane.

GROUP IV.

Group 4th comprises Iron, Manganese, Chromium, Cobalt and Nickel. The members of this group, like those of the last, constitute an extremely well defined natural family. The types of their combinations with the members of group 1st are numerous, and it is in this respect that they differ from

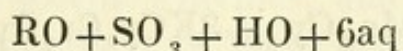
the elements constituting group 3d, with which, as already observed, their connection is very intimate. These types are as follows:



Corresponding to which we have

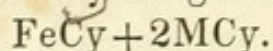
MnO.	Mn ₂ S--MnO--MnO ₂ --MnO ₃ --Mn ₂ O ₃ --Mn ₂ O ₇ --Mn ₂ O ₅ --Mn ₃ O ₄
FeO.	? FeO--FeS ₂ --FeO ₃ --Fe ₂ O ₃ --? ? Fe ₃ O ₄
CrO.	? CrO--? CrO ₃ --Cr ₂ O ₃ --? ? ?
CoO.	? CoO--CoS ₂ ? Co ₂ O ₃ --? ? Co ₃ O ₄
NiO.	Ni ₂ S--NiO--NiS ₂ ? Ni ₂ O ₃ --? ? ?

In their general chemical relations the five members of this group very strongly resemble each other. They all form protoxides which are powerful bases and the similar salts of which are isomorphous. The most interesting of these salts is a class of sulphates constituted according to the general formulæ

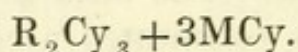


isomorphous, and capable of forming double salts with the sulphates of soda and potassa, in which one equivalent of either of these last replaces the one equivalent of constitutional water in the original salt. The sesquioxides of the members of this group form also by uniting with acids, several very remarkable series of compounds, which like the salts of the protoxides are isomorphous. Chromium, manganese and iron form acids by uniting with three equivalents of oxygen. Of these the chromic acid is the most stable, the man- ganic acid less so, the ferric acid is decomposed by the slight- est causes. The other two elements, cobalt and nickel, do not form acids at all, so far at least as we at present know. Here the law of grades is distinctly shown. Manganese again forms two distinct acids with oxygen, to which the other mem- bers of the group offer no parallel. The number of com- pounds formed by manganese is moreover greater than the number of those formed by any one of the other members of the group. For these reasons we place manganese at the head of the group, and may without impropriety give its name to the whole family. The members of this group unite with cyanogen to form a remarkable series of compounds, which

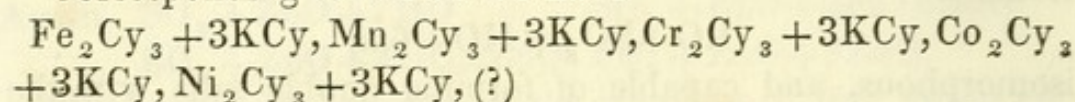
by their union as cyan-acids with cyano-bases, form a series of salts, the elements of which are united by most powerful affinities. Of these cyano-salts there are two classes; in the first class, a protocyanide of a metal of group four, acts as an acid towards the cyanides of other radicals; in the second class of salts a sesquicyanide of a metal belonging to group four, acts as an acid towards the cyanides of other radicals or of other metals belonging to the same group. Belonging to the first of these classes of salts we have but one series, viz: the cyano-ferrites represented by the general formula



The second class of salts is more numerous and is represented by the formula



Corresponding to which we have



The members of this group are connected with those of group 1st, by several distinct and well ascertained isomorphisms. Thus the chromic and manganic acids form salts which are isomorphous with the corresponding sulphates and seleniates. The chromates moreover resembles the sulphates in solubility and in their mode of forming double salts. Again, a peculiar acid of manganese has occasionally been obtained in combination with potassa, forming a salt, the formula of which is $\text{Mn}_2\text{O}_5 + \text{KO}$, and which is isomorphous with chlorate of potassa $\text{ClO}_3 + \text{KO}$. Still farther, the salts of hypermanganic acid are isomorphous with the corresponding salts of hyperchloric acid $\text{Mn}_2\text{O}_7 + \text{RO}$ with $\text{ClO}_7 + \text{RO}$. Hence it is clear that, in combination at least, two equivalents of manganese replace and are isomorphous with one equivalent of chlorine. And thus group 1st and 4th are connected by a two-fold isomorphism. We may here observe that as one equivalent of manganese is in combination isomorphous with one equivalent of sulphur, two equivalents of manganese ought to be isomorphous with two equivalents of sulphur, consequently the salts of manganese of the type $\text{Mn}_2\text{O}_5 + \text{RO}$, which from analogy we will

call hypomanganates, should be found isomorphous with the hyposulphates, $S_2O_5 + RO$, and the hyposulphates should therefore be isomorphous with the chlorates. We have noticed this point because the attention of chemists does not seem to have been directed towards it, obvious as it may appear. The salts of the protoxides of this group are isomorphous with the similar salts of the protoxides of group 3d, and there is furthermore a very great analogy in other respects between the salts of the two series of oxides. All the metals of group 4th dissolve in hydrated acids by a simple replacement of hydrogen, and the three types of the compounds of group 3d correspond to the first three types of the compounds of group 4th, with the basacigen family.

The metals composing this group possess nearly the same atomic weights and specific gravities, and further researches may perhaps identify them in these respects. The specific gravity of chromium however differs greatly from the mean specific gravity of the other four metals. The mean of the atomic members of iron, cobalt, manganese and nickel, is .2896, and the mean atomic volume is consequently $\frac{1}{.2896}$ or

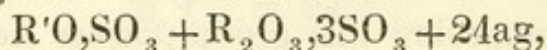
3.4530. It is worthy of notice that the molecules of these four metals are smaller than those of any other simple substance with which we are acquainted.

Finally, iron and nickel are the only two substances which are certainly known to be susceptible of magnetism, though cobalt and manganese have been supposed to share this property also; the equivalents of the two former we may also remark have the same specific heat.

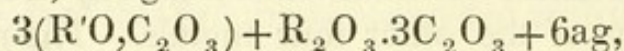
GROUP V.

The fifth group comprises Aluminum, Glucinum and Zirconium. These three elements are nearly related to those of group four, and are classed with them by Graham and by Kane. They differ however essentially from them in forming but a single molecular type by combining with the members of group 1st. This type is represented by the formulæ R_2A_3 .

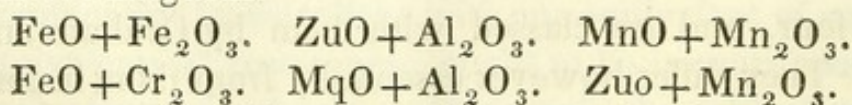
The sesquioxides, alumina, glucina and zirconia, are capable of acting the part of acids toward metallic protoxides as well as of powerful bases toward the strong acids. The salts of alumina and glucina are probably isomorphous with those of zirconia, though this point has not yet been satisfactorily ascertained, they are however certainly isomorphous with the sesquioxides of the members of group four, both in a free state and in a state of combination. Alumina frequently replaces the sesquioxides of iron in mineral compounds as well as in artificially prepared salts. As an instance of the striking analogy between the chemical relations of the sesquioxides of groups four and five we may cite the general formulæ of the alum family.



corresponding to which we have the alumina, iron, manganese and chrome-alums. In like manner we have a class of double oxalates, the general formulæ of which is



corresponding to which we have double oxalates of chromium, aluminum, and iron with oxalates of potassa, which are like the alums isomorphous. The elements which we have arranged under group 5th are connected with the basacigen family, and with the members of group 3d, indirectly by their relation with group 4th. The three last groups, viz: groups 3d, 4th, and 5th, constitute in a great measure the 2d or magnesian class of Graham. They are, as we have already stated, very intimately connected, as well by chemical as by physical properties, though we have thought it more in accordance with the true principles of a natural classification, to arrange them under three separate classes or groups. As an illustration of their capacity of replacing one another in combination, we cite the following formulæ derived for the most part from the mineral kingdom.

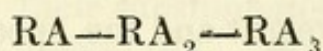


We may remark in conclusion that aluminum is isomeric with iron and manganese $13.72 \times 2 = 27.44$, and that the equiv-

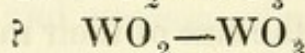
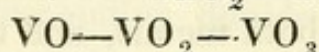
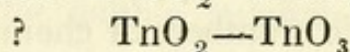
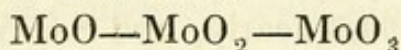
alent of glucinum so nearly approaches that of the other members of the two groups, viz: the 4th and 5th, that we may reasonably expect that upon more accurate investigation, it will be found isomeric with them. The equivalent of zirconium is however entirely removed from the series and approximates toward that of zinc.

GROUP VI.

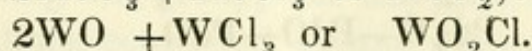
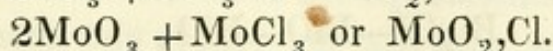
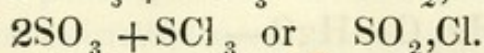
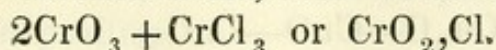
The sixth group comprises four elements, Molybdenum, Tungsten, Vanadium, Columbium. The compounds of these elements with the members of group 1st may be arranged under three types.



corresponding to which we have



It will be immediately observed that these types are, so far as they extend, precisely similar to those of group 4th. Several of the salts of tungstic and molybdic acids are isomorphous, while on the other hand, one of the forms of chromate of lead corresponds with that of the molybdate of the same base. Between the vanadic and chromic acids there is also considerable resemblance, though their compounds are not known to be isomorphous. There exist, moreover, compounds of Molybdenum and Tungsten with oxygen and chlorine, precisely analogous in composition to the so-called chloro-sulphuric and chloro-chromic acids, thus we have



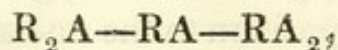
Formulae, which together with the analogies which we have already mentioned, connect this group very evidently with the 4th, and indirectly with the 1st, 3d, and 5th groups. The protoxides of Vanadium and Molybdenum are not powerful

bases like those of group 4th, neither do the four metals composing this group form with the basacigen family sesqui-compounds as do all the members of group four. Molybdenum forms with sulphur a higher acid than the sulphy-molybdic, the formulæ being MoS_4 , and thus apparently connects this group with group 2d; the compounds of this acid with sulphur-bases are well worthy of attention, only one compound, the potassium-salt $\text{MoS}_4 + \text{KS}$, being at present known. The chemical properties and relations of the four elements which we have associated together as group 6th are in general very similar, though further researches are wanting to enable us to assign with certainty the proper position of columbium.

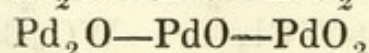
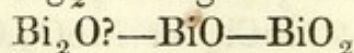
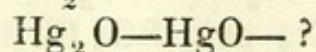
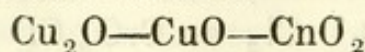
Both the atomic weight and the specific gravity of Tungsten are very nearly double those of molybdenum, thus, $2\text{Mo} = 95.92 = \text{W} = 94.8$ nearly, and $\text{S.G.W} = 17.22 = 2\text{S.G.Mo} = 17.23$. The atomic numbers or chemical densities are consequently the same for both metals, and they likewise agree in atomic volume, or in the size of their molecules. The mean atomic number is .1811, and the mean atomic volume 5.52. The specific gravities of vanadium and columbium are as yet unknown.

GROUP VII.

Group 7th comprises Copper, Mercury, Bismuth, and Palladium. The types of the compounds formed by the members of this group with those of group 1st are three in number.



corresponding to which we have



In their general relations the four metals composing group 7th, agree in a remarkable manner, though there exist between their compounds no observed isomorphisms. Their corresponding oxides are all insoluble in water; the suboxides of

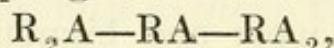
copper, mercury and palladium forming definite and exceedingly well marked salts with acids, a property, it may be remarked, which is rare in oxides of that constitution. The protoxides of each is in like manner a powerful base, while the pertoxides of copper, bismuth and palladium are analogous in instability and in incapacity to form well defined compounds with either acids or bases. The protoxides of copper, bismuth and mercury exhibit moreover a remarkable tendency to form compounds containing an excess of base. The subnitrates of copper and bismuth are analogous in composition, according to Graham, being— $\text{NO}_5, \text{HO} + 3\text{CuO}$ and $\text{NO}_5, \text{HO} + 3\text{BiO}$; their subsulphates also agree in composition if we omit basic water, thus, $\text{SO}_3 + 3\text{CuO}$ and $\text{SO}_3 + 3\text{BiO}$. Group 7th is connected with groups 3d and 4th by the isomorphism of the double sulphate of copper and potassa with the corresponding double sulphates of zinc and potassa, and of iron and potassa, thus we have $\text{CuO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6\text{aq}$ isomorphous with $\text{ZnO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6\text{aq}$ and $\text{FeO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6\text{aq}$. The double cyanide of mercury and potassium is moreover isomorphous with the double cyanide of zinc and potassium $\text{HgCy} + \text{KCy}$ with $\text{ZnCy} + \text{KCy}$, both these salts appearing in octohedrons of the regular system. Bismuth is associated with the 2d or nitrogen group by Dr. Kane, on the ground of the isomorphism of its sulphide with the tersulphide of Antimony, yet as its oxides do not form well defined salts with alkaline bases, and as it does not form with hydrogen the characteristic gaseous compound of the type RH_3 , we cannot admit the propriety of displacing it from its original position.

No isomerism exists between the equivalents of the four elements composing this group, nor are their atomic numbers and atomic volumes connected by any very certain and definite relations. The atomic numbers of the four metals are as follows: Copper = .2742, Mercury .1321, Bismuth .0922, Palladium .2153, taking the number for Copper as unity, the number for the other metals will be to it nearly in the follow-

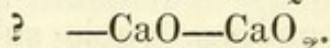
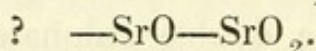
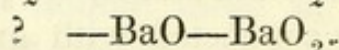
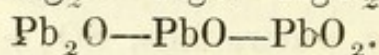
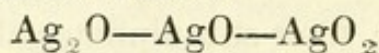
ing ratios, mercury $\frac{1}{2}$, bismuth $\frac{1}{3}$, palladium $\frac{1}{9}$, and the atomic volumes will of course be in the inverse ratio, viz : copper 1, mercury 2, bismuth 3, palladium 12.

GROUP VIII.

The 8th group of our classification comprises 5 elements, viz : Barium, Strontium, Calcium, Lead and Silver. The types of the compounds of the members of this group with the members of group 1st, are three in number.



corresponding to which we have



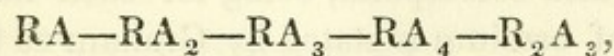
The similarly constituted salts of barium, strontium and lead are isomorphous and agree remarkably in solubility in water and in their purely chemical relations. Thus the sulphates of these three elements occur in nature crystallized in the same form, and when artificially prepared agree in their insolubility in appearance, and in their chemical properties. In like manner the nitrates of lead, barium and strontium are isomorphous and similarly constituted. Calcium is connected with the other members of this group, by the isomorphism of one of the forms of its carbonate, viz : arragonite, with the carbonates of baryta and strontia, by the insolubility of its sulphate, and by a general similarity in chemical relations. We may also add, that agreeably to the researches of Newmann, the specific heats of the equivalents of the Carbonates of Lime, Baryta, strontia and lead are the same, and that the same relation of equality holds good for the specific heats of the sulphates of the same basis. Silver was first classed with lead by Dr. Kane, and the two metals agree very closely in chemical properties, in the insolubility of their chlorides, bromides and iodides, &c., but their salts are not connected by any known isomorphisms. On the whole then we may regard this group

as being extremely well defined and as presenting a fair example of a Natural family in Chemistry. With groups 3d and 4th this family is connected by the isomorphisms of the carbonates of strontia and baryta, with one of the forms of the carbonates of magnesia and of iron, by the isomorphism of the ordinary carbonate of lime or Iceland spar with the usual forms of the carbonates of iron and magnesia, and by the analogy in constitution and in form of sulphates of iron and of lime whose formulæ are $\text{SO}_3 + \text{FeO} + 2\text{HO}$ and $\text{CaO} + \text{SO}_3 + 2\text{HO}$. The relations between this group and group 1st are in the present state of our knowledge indirect, being traced chiefly through groups 3d and 4th.

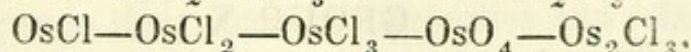
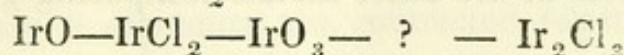
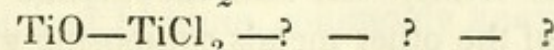
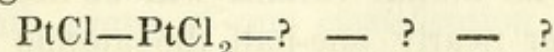
No isomerisms subsist between the equivalents of the elements constituting this group. The atomic numbers and atomic volumes of silver and of lead, the only members of the group for which they can at present be determined, are also unconnected by any simple ratios. The specific heat of the atom of silver is double that of lead, and the former metal is apparently more highly electro-negative than the latter.

GROUP IX.

Group 9th comprises Platinum, Titanium, Iridium and Osmium. The complete series of the compounds formed by the members of this group with those of group 1st are 5 in number, viz :



corresponding to which we have



The four elements which we have arranged under group 9th, correspond for the most part very closely in chemical properties and relations. The bichlorides of all these metals form with chloride of potassium, highly characteristic chloro-salts which crystallize in regular octahedrons. Their general

formula is $RCl_2 + KCl$. The corresponding compounds of platinum, iridium and osmium are all isomorphous. None of the protoxides of this group are very powerful bases and their binoxides like compounds of that type generally, are capable of uniting to a certain extent with both acids and bases.

With the 7th, or copper family, this group is connected by the isomorphism of the corresponding salts of the chloropalladious, and chloropalladic acids with the chloroplatinous and chloroplatinic acids.

With group 2d this group is connected by the analogy in composition of osmic acid with hypo-nitric and hypo-antimonic acids. With group 4th this group may possibly be connected by the analogy of the sesquichlorides of iridium and osmium to the sesquichlorides of iron and manganese.

Of the four metals composing this group platinum and iridium are certainly isomeric, the equivalent of each being 98.84. The equivalent of osmium, viz : 99.72, nearly approaches that of platinum and iridium as to lead to the suspicion that more accurate researches will establish their identity. Finally the equivalent of Titanium as at present received is almost exactly one-fourth of the equivalent of Platinum and Iridium— $24.5 \times 4 = 98.00$.

The atomic numbers of platinum, iridium, and titanium are also equal, the mean being .2179; the atomic volumes consequently also correspond, being for each 4.59. The specific gravity of osmium is stated by Graham as being "about 10," in this case its atomic volume will be nearly twice and its atomic number nearly one-half the atomic volumes and atomic numbers of the other metals composing group 9th.

GROUP X.

Group 10th comprises Gold, Uranium, Rhodium and Tin. The types of the compounds formed by the members of this group with the first or basacigen family are four in number, viz: $R_2A - RA - RA_2 - R_2A_3$ corresponding to which we have, $Au_2O, Au_2O_3, UC - U_2O_3 - R_2O_3 - SnO - SnO_2 - Sn_2O_3$.

The sesquioxides of all these metals agree in being feebly acid and basic; that of tin has as yet been but imperfectly examined. The sesquichlorides of gold, uranium and rhodium, form well characterized chloro-salts with the chlorides of the alkaline metals. This group is connected with the last by the isomorphism of the chlorostannates and chloroplatinates of potassium, $\text{SnCl}_2 + \text{KCl}$ and $\text{PtCl}_2 + \text{KCl}$; by the isomorphism of the native dioxides of tin and titanium, SnO_2 and TiO_2 , and by the analogy of the sesquichlorides of gold, uranium and rhodium, with those of osmium and iridium.

Between the elements composing this group no probable isomerism exists, though the atomic weight of gold, as stated by Graham, is nearly identical with that of osmium, as at present received. The atomic number of gold is identical with that of silver, with which metal gold is isomorphous in the metallic state; but the analogy between the two metals ceases here.

The atomic number of rhodium closely approximates to that which we have stated for the last group, with which therefore it is in this way connected. The atomic number of uranium is remarkable as being very small, viz: .0414; its atomic volume is consequently larger than that of any metal yet described, viz: 24.15.

Finally the specific heats of the equivalents of gold and tin agree with each other and with that of platinum.

GROUP XI.

The eleventh group of our classification comprises Potassium, Sodium, and Lithium, commonly known as the alkaline metals. These 3 elements are connected together by very strong analogies in their chemical properties and relations, but not by any well established isomorphisms. Their isomorphism in the metallic state appears tolerably certain. The most energetic affinities are exerted by the protoxides of these metals; the greater number of the salts which they form with oxy-acids are soluble in water and neutral in composition,

and their relations to other oxides are almost invariably those of bases to acids. With group 8th they are connected by the isomorphism of the sulphate of soda with sulphate of silver. Under certain circumstances an equivalent of potash or soda may be replaced in combination by an equivalent of Lime + an equivalent of water, or $\text{CaO} + \text{HO}$, and thus this group is connected with group 8th and 4th at the same time. Again we find that one equivalent of nitrogen + four equivalents of hydrogen are capable of replacing potassium in combination without change of form, NH_4 being isomorphous with K, and thus this group is connected with Groups 2d and 3d.

No isomerism appears to subsist between the equivalents of the members of this group. The atomic number of potassium is very nearly double that of sodium, and its atomic volume is consequently one half that of the latter metal. The specific gravity of lithium appears not to have been determined, its atomic weight is very remarkable as being lower than that of any other metal, unless indeed hydrogen be regarded as such.

GROUP XII.

The twelfth group comprises 2 elements—Yttrium and Thorium. The compounds of these two metals are as yet very imperfectly known. Their oxides are regarded as protoxides, and bear considerable analogy to each other in chemical properties and relations. No definite relations have been established between them and the members of any other group.

GROUP XIII.

Group 13th comprises Cerium, Lanthanium, Didymium, Erbium and Terbium. Our knowledge of these substances is as yet too much imperfect to admit of our entering into their relations and properties, sufficiently to establish their position in the same class. They all occur in nature in the same minerals and are exceedingly difficult to separate from one another, by chemical means. The last four in the order which we

have mentioned, have been discovered by Mosander within a few years, and are yet under his investigation.

GROUP XIV.

Group 14th comprises Carbon, Boron and Silicon. These elements are associated together by Graham upon the ground that they exhibit a general resemblance to one another without any precise relations. Independently, however, of the non-agreement of the types of their compounds with the basigen group, carbon enters into the constitution of an immense number and variety of compounds, to which boron and silicon offer no parallels. If however we reduce the received equivalents of boron and silicon by one-third, as proposed in the case of silicon by Dr. Clarke, the silicic and boric acids become analogous in constitution to carbonic acid, SO_2 and BO_2 to CO_2 . This view of the constitution of the two former acids is supported by their general analogy to carbonic acid in chemical relations, they are feeble acids, and are at the same time capable of entering into combination with bases in many proportions. Moreover, the formulæ of the compounds of boron and silicon generally, become much more simple by making the proposed change, than they are at present, as will readily be seen from a comparison of the following formulæ, which we have calculated for the purpose.

OLD VIEW.

	$2\text{SiF}_3 + 3\text{KFl},$
	$2\text{BF}_3 + 3\text{KFl},$
	$3\text{NaO} + 2\text{BO}_3,$
Biborate of Soda Borax.	$\text{NaO} + 2\text{BO}_3,$
	$\text{NaO} + \text{BO}_3,$
Boracite.	$3\text{MgO} + 4\text{BO}_3,$
Picrosmine.	$3\text{MgO} + 2\text{SiO}_3,$
Pyroxene.	$3\text{MgO}, 2\text{SiO}_3 + 3\text{CaO}, 2\text{SiO}_3$
Steatite.	$3\text{MgO}, 2\text{SiO}_3 + \text{Al}_2\text{O}_3, 2\text{SiO}_3, 6\text{HO}$
Amphigen or Analcime.	$3\text{RO}, 2\text{SiO}_3 + \frac{1}{3}(\text{Al}_2\text{O}_3, 2\text{SiO}_3) \pm \text{aq}$
Felspar, Albite, Stilbite.	$\text{RO}, \text{SiO}_3 + \text{Al}_2\text{O}_3, 3\text{SiO}_3 \pm \text{aq}.$

NEW VIEW.

	$\text{SiF}_2 + \text{KF}$, (Clark.)
	$\text{BF}_2 + \text{KF}$,
	$\text{NaO} + \text{BO}_2$
Biborate of Soda Borax.	$\text{NaO} + 3\text{BO}_2$
	✓ $2\text{NaO} + 3\text{BO}_2$ like $2\text{NaO} + 3\text{CO}_2$.
Boracite.	$\text{MgO} + 2\text{BO}_2$
Picrosmine.	$\text{MgO} + \text{SiO}_2$
Pyroxene.	$\text{MgO}, \text{SiO}_2 + \text{CaO}, \text{SiO}_2$ like $\text{MgO},$ $\text{CO}_2 + \text{CaO}, \text{CO}_2$. Dolomite.
Steatite.	$\text{MgO}, \text{SiO}_2 + \text{Al}_2\text{O}_3, 3\text{SiO}_2 + 6\text{HO}$
Amphigen or Analcime.	$\text{RO}, \text{SiO}_2 + 2(\text{Al}_2\text{O}_3, 3\text{SiO}_2) \pm \text{aq}$
Felspar, Albite, Stillite.	$\text{RO}, 3\text{SiO}_2 + \text{Al}_2\text{O}_3, 3\text{SiO}_2$.

The formulæ of other borates and silicates are not however always rendered more simple by the proposed change in the equivalents of boron and silicon, so that the expediency of such a change must remain for the present undecided, and we must admit, that, as in the case of the last group, further researches are wanting, before we can assign with any degree of probability, the proper places of the elements, carbon, boron and silicon.

Thus far then we have endeavoured to display the analogies which subsist between the elementary bodies. We have divided them into natural families or groups, according to our idea of the true principles which must govern every attempt to create a natural classification in any branch of science whatever. In a word, we have endeavoured to rely upon *general* and not upon particular, analogies, and our classification consequently differs for better or for worse from every one which has yet been proposed. The merit of having first suggested such a mode of classification belongs to the English chemist, Graham, who, in his recent treatise upon Chemistry, has divided the elements into eleven classes, depending chiefly upon their isomorphous relations. We will here quote the classes of Graham in a column over our own.

GRAHAM.

- 1st Class. Oxygen, Sulphur, Selenium, Tellurium
 2d Class. Mg—Ca—Mn—Fe—Co—Ni—Zn—Cd—Cu—H—
 Bi—Cr—Al—Gl—V—Zn—Y—Th.
 3d Class. Barium, Strontium, Lead.
 4th Class. Potassium, Sodium, Ammonium, Silver.
 5th Class. Chlorine, Iodine, Bromine, Fluorine.
 6th Class. Nitrogen, Phosphorus, Arsenic, Antimony.
 7th Class. Tin, Titanium.
 8th Class. Gold, Silver.
 9th Class. Platinum, Palladium, Iridium, Osmium.
 10th Class. Tungsten, Molybdenum.
 11th Class. Carbon, Boron, Silicon.
 Unclassified. Mercury, Cerium, Columbium, Rhodium, Uranium, Lanthanum, (Erbium and Terbium.)
-

- 1st Class. Oxygen, Sulphur, Selenium, Tellurium, Chlorine, Iodine, Bromine, Fluorine.
 2d Class. Phosphorus, Nitrogen, Arsenic, Antimony.
 3d Class. Hydrogen, Zinc, Cadmium, Magnesium.
 4th Class. Iron, Manganese, Cobalt, Nickel, Chromium.
 5th Class. Aluminum, Glucinum, Zirconium.
 6th Class. Molybdenum, Tungsten, Vanadium, Columbium.
 7th Class. Copper, Mercury, Bismuth, Palladium.
 8th Class. Barium, Strontium, Calcium, Lead, Silver.
 9th Class. Platinum, Titanium, Iridium, Osmium.
 10th Class. Gold, Uranium, Rhodium, Tin.
 11th Class. Potassium, Sodium, Lithium.
 12th Class. Yttrium, Thorium.
 13th Class. Cerium, Lanthanum, Didymium, Erbium, Terbium.
 14th Class. Carbon, Boron, Silicon.

We are likewise indebted to the suggestions of Dr. Kane, for several important changes in the original classification of Graham: thus lead and silver were first associated together by the Irish chemist, as were also palladium and copper.

With certain other changes proposed by Kane we do not coincide, as they are entirely opposed to our convictions of truth.

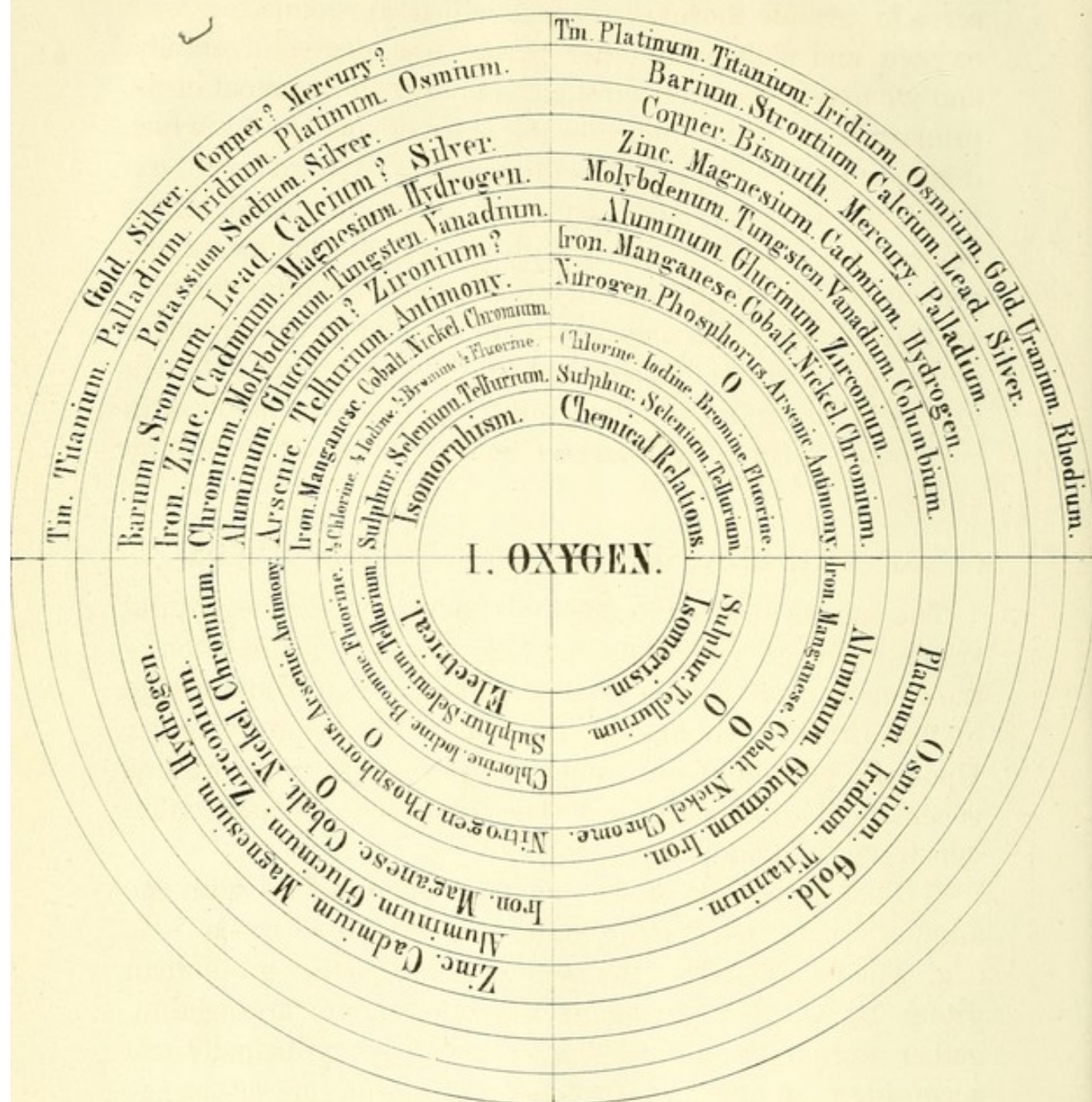
The tendency of discovery, in our time, is to connect the different groups and the individual members of which they are composed more and more closely together. Every year fills up some separating chasm, brings to light new analogies, and impresses us yet more strongly with the belief that nature in truth, is one in essence, though many in form. Perhaps it will hereafter be found that those bodies which we term elements are in reality compound; that they are the resultants of a few elementary forces, themselves perhaps but modifications of a single primary force. The very idea of matter, reduced to its simplest form, is the idea of resistance, and the idea of resistance, think of it as we may, is only one form of the idea of force. To us and to our nature, an atom is a sphere of force to whose centre we cannot get. This view of the constitution of matter, will at least afford us some explanation of those analogies which now seem so difficult to comprehend; for the resultants of the same forces must of necessity bear some relation and proportion to one another; and it seems to us at least, that the assumption of a few primary forces, whose innumerable modifications and modes of action, produce all the phenomena of material bodies with which we are acquainted, enables us to form a simpler and a clearer idea of the unity of nature than any hypothesis which has yet been proposed.

To exemplify at a glance the relations of the several groups to each other, and to show, at the same time, in what manner the elements form a natural scale of gradation, we propose to make use of an artifice often adopted by naturalists, and for the suggestion of which the writer is indebted to Dr. Torrey.

Assuming a single element, oxygen for example, as a centre, we may draw around it a circle of any convenient radius, and we may divide this circle into segments, each segment corresponding to some particular point of analogy.

Concentric with this primary circle, and separated from it by

SCHEME OF ANALOGIES.



a short interval of radius, we may draw another which shall serve to include those substances which are connected with oxygen and with each other by the first degree of affinity, and we may place each substance opposite the segment of the primary circle which indicates the point of analogy by which it is most closely connected with oxygen. A third circle, external to, and concentric with the last, will include those bodies which are connected with oxygen by the second degree of analogy, and so on for other circles. Blank segments, or blank circles will indicate want of analogy in particular points or in entire degrees. And thus we shall obtain a graphical illustration of the connection of the elements with each other, and of the degree of analogy between the several groups.

OF THE CLASSIFICATION OF COMPOUNDS.

The classification of compounds, according to the natural system, obviously depends upon the previous classification of the elements, and follows readily and easily from a knowledge of the arrangement and relations of the elementary groups. Upon this portion of our subject we propose to be as brief as is consistent with clearness. The principles of classification which we shall adopt are as follows:

1. The compounds of the members of group 1st with one another are arranged according to their molecular types.
2. The compounds of the members of any other group than group 1st with the members of group 1st, are arranged together in groups according to molecular types, principally and according to isomorphism, wherever isomorphisms subsist.

For example, we classify together the Protoxides, Proto-sulphides, Proto-selenides, Proto-tellurides, Proto-chlorides, Protiodides, Proto-bromides, and Proto-fluorides of the members of each natural group of elements. Supposing, for example, that a particular natural group contains four elements, we should have of course a group of proto-amphides of this elementary group, consisting of $4 \times 8 = 32$ individuals. These

again we subdivide into eight sub-groups, each sub-group consisting (in this particular instance) of four individuals. The sub-groups are arranged according to their electro-negative or chlorous constituent, so that we thus associate together in the same sub-group, all the protoxides of a particular class of elements; in another sub-group all the proto-sulphides of the same class of elements, and so on.

The same principle is applied to the classification of deuto-amphides, sesqui-amphides, and so forth.

As examples of this method of arrangement, we will give a few groups and sub-groups of different molecular types.

THIRD GROUP OF ELEMENTS.

Zinc, Cadmium, Magnesium, Hydrogen.

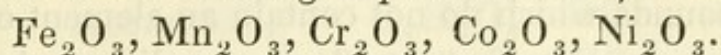
GROUP OF PROTO-AMPHIDES.

Sub-group 1st.	Sub-group 2d.	Sub-group 3d.	Sub-group 4th.
ZnO	ZnS	ZnSe	ZnTe
CdO	CdS	CdSe	CdTe
MgO	MgS	MgSe	MgTe
HO	HS	HSe	HTe
Sub-group 5th.	Sub-group 6th.	Sub-group 7th.	Sub-group 8th.
ZnCl	ZnI	ZnBr	ZnF
CdCl	CdI	CdBr	CdF
MgCl	MgI	MgBr	MgF
HCl	HI	HBr	HF

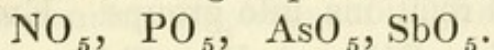
As the members of the 3d group of elements do not form very distinct compounds with more than one equivalent of a member of the first or amphigen group, we must refer to some other one of the elementary groups for further illustrations. It will be immediately observed in the example which we have already given, that the Protoxides of group 1st constitute together a natural family or sub-group, the protosulphides a second sub-group and so on; hence in a descriptive work, the sub-groups should be treated of in succession, first by a general account of their properties and relations, and secondly by

the special description of the individuals of which each sub-group is composed.

Another example of a natural *sub-group* is furnished by the sesquioxides of the fourth group of elements, viz :



Again we have as a sub-group of another type,



Again, $\text{PbCl}_2, \text{IrCl}_2, \text{OsCl}_2, \text{TiCl}_2.$

From this principle of classification it follows that we shall have for each group of elements, several groups of compounds, with the members of group 1st, the number depending on the number of the different types of the compounds formed by the two groups with each other.

Thus, if a particular group of elements form with the 1st or Amphigen group, compounds of the types, $\text{RA}, \text{RA}_2, \text{R}_2\text{A}_3, \text{RA}_3$, it is clear that we shall have four groups of compounds, namely :

1. Proto-amphides RA
2. Deuto-amphides RA_2
3. Sesqui-amphides R_2A_3
4. Ter-amphides RA_3

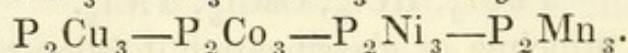
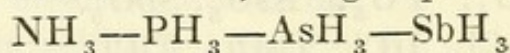
Each of these groups will then be subdivided into eight sub-groups, as follows :

GROUP 1st, Proto-amphides.		GROUP 2d, Deuto-amphides.	
Sub-group 1st, Protoxides	RO	1st, Deutoxides	RO_2
Sub-group 2d, Proto-sulphides	RS	2d, Deuto-sulphides	RS_2
Sub-group 3d, Proto-selenides	RSe	3d, Deuto-selenides	RSe_2
Sub-group 4th, Proto-tellurides	RTe	4th, Deuto-tellurides	RTe_2
Sub-group 5th, Proto-chlorides	RCl	5th, Deuto-chlorides	RCl_2
Sub-group 6th, Prot-iodides	RI	6th, Deut-iodides	RI_2
Sub-group 7th, Proto-bromides	RBr	7th, Deuto-bromides	RBr_2
Sub-group 8th, Proto-fluorides	RF	8th, Deuto-fluorides	RF_2

GROUP 3d, Sesqui-amphides.		GROUP 4th, Teramphides.	
Sub-group 1st, Sesqui-oxides	R_2O_3	1st, Teroxides	RO_3
Sub-group 2d, Sesqui-sulphides	R_2S_3	2d, Tersulphides	RS_3
Sub-group 3d, Sesqui-selenides	R_2Se_3	3d, Terselenides	RSe_3
Sub-group 4th, Sesqui-tellurides	R_2Te_3	4th, Tertellurides	RTe_3

Sub-group 5th, Sesqui-chlorides	R_2Cl_3	5th, Terchlorides	RCl_3
Sub-group 6th, Sesqui-iodides	R_2I_3	6th, Teriodides	RI_3
Sub-group 7th, Sesqui-bromides	R_2Br_3	7th, Terbromides	RBr_3
Sub-group 8th, Sesqui-fluorides	R_2F_3	8th, Terfluorides	RF_3

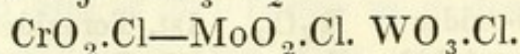
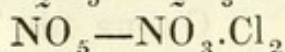
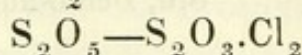
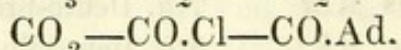
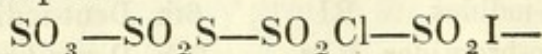
3. Compounds which do not contain an element of the amphigen group are classified together, according to their constitution and general relations, into groups. Examples,



With the exception of ammonia, the carburets of hydrogen, and one or two other substances which we shall hereafter notice, our knowledge of the compounds of the non-amphigen groups is as yet too imperfect to admit of our entering upon any generalizations concerning them.

4. Before entering upon the subject of the classification of double compounds, it is necessary to make a few remarks, concerning the substitutions of the elements generally, and more particularly concerning the substitutions of the members of the amphigen group for one another.

We admit then generally that the members of *any* group are capable of replacing one another in equivalent proportions, without destroying the type of the particular compound in which the replacement occurs, though the chemical relations of the new compound may or may not be the same with those of the original from which it is derived. We therefore classify compounds thus derived by substitution with those from which they are derived, provided that the chemical relations of the primitive and its derivatives are not absolutely incompatible. Examples.



Under certain circumstances, bodies belonging to different groups are capable of replacing one another in combination

without altering either the molecular type or the general relations of the primitive. Such derivatives are of course to be classified with their primitives. Example.

Acetic acid, $C_4H_3O_3 + HO$.

Chloracetic acid, $C_4Cl_3O_3 + HO$.

5. Finally, the similar amphides of *different* groups may be so nearly related in chemical properties, as to be placed under the same natural group or sub-group of compounds. Examples.

The protoxides of groups 3d and 4th, viz :

$ZnO, MgO, HO, CdO, FeO, MnO, CoO, NiO, CrO$.

The sesquioxides of groups 4th and 5th, viz :

$Fe_2O_3, Mn_2O_3, Co_2O_3, Ni_2O_3, Cr_2O_3, Al_2O_3, Cl_2O_3, Zr_2O_3$.

The bichlorides of groups 7th, 9th and 10th, viz :

$PdCl_2, PtCl_2, IrCl_2, OsCl_2, TiCl_2, SnCl_2$.

The teroxides of groups 1st, 4th and 6th, viz :

$SO_3, SeO_3, TeO_3, CrO_3, MnO_3, VO_3, WO_3, MoO_3$.

Certain oxides of groups 1st and 4th, viz :

$S_2O_5, ClO_5, Mn_2O_5 - ClO_7, Mn_2O_7$.

6. Double compounds, that is to say, bodies composed of two others, each of which is itself a compound, are classified in a manner analogous to that just described for single compounds, the classification depending mainly upon the electro-negative or chlorous compound constituent.

Those double compounds whose constituents are members of the same natural groups of single compounds are classified together as a natural group of salts, and this group of salts is again subdivided into eight sub-groups, comprising

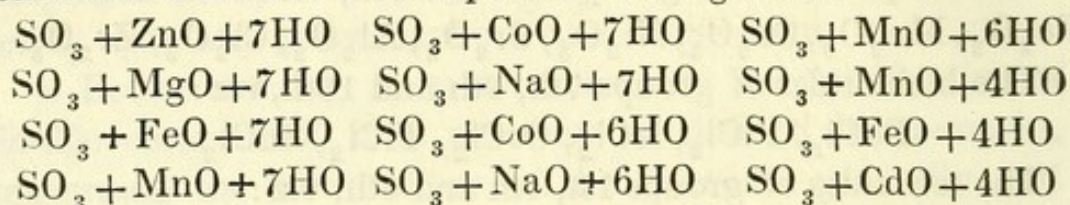
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|-------------------|------------------|
| 1. Oxy-salts, | 5. Chloro-salts, |
| 2. Sulphur-salts, | 6. Iodo-salts, |
| 3. Selenio-salts, | 7. Bromo-salts, |
| 4. Telluri-salts, | 8. Fluo-salts, |

wherein the term salt is applied exclusively to the compounds of bodies relatively acid with bodies relatively basic. For example,

SO_3 , SeO_3 , TeO_3 , CrO_3 , MnO_3 , MoO_3 , WO_3 ,
 belonging to the same sub-group of acids, and

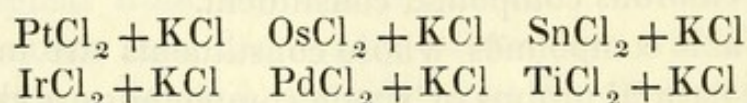
ZnO , MgO , CdO , HO , FeO , MnO , CoO , NaO , CrO ,
 belong to the same sub-group of bases, consequently the similarly constituted compounds of these acids and bases form together a natural sub-group of salts, according to the principles which we have adopted. The 63 salts which would thus be formed, are subdivided into 7 genera, viz : sulphates, seleniates, tellurates, chromates, manganates, molybdates, and tungstates.

As the sulphates alone have been carefully studied, we will cite from them a few examples of saline genera.



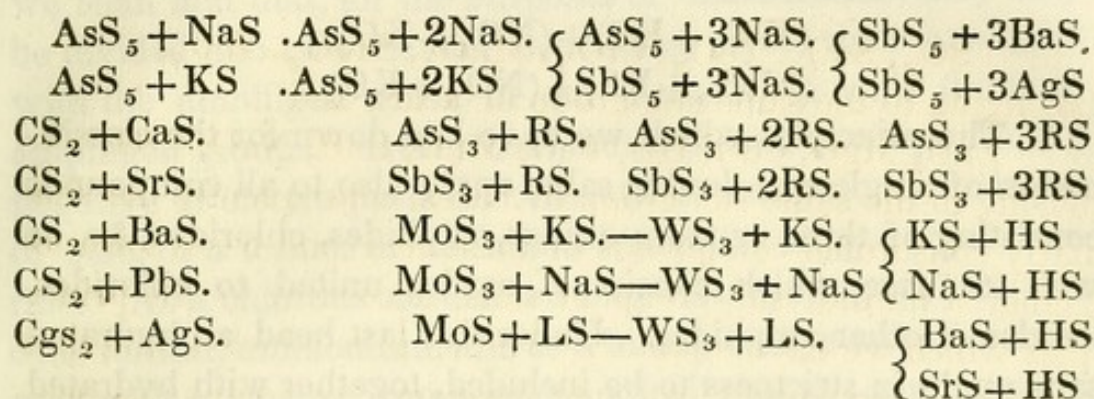
In these instances the sulphates are all hydrated, and ought therefore to be regarded as triple compounds. Their formulæ however suffice to exhibit their analogies and the propriety of placing them in the same genus. The peculiarity of their constitution in containing an atom of constitutional water has already been alluded to.

As further examples of natural sub-groups of salts we may cite

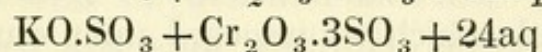
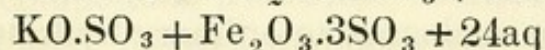
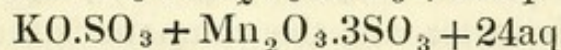
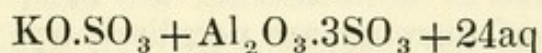


which series of salts is arranged according to base, in consequence of our imperfect knowledge of the other acids belonging to the same group with the chloracids in the formulæ. The individuals of this genus are isomorphous.

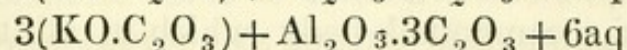
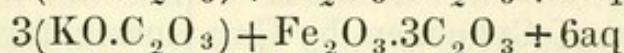
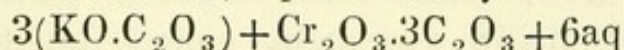
The sulphur-salts are for the most part analogous to the oxy-salts containing the same radicals. As these two classes of salts have been more extensively and carefully studied than any others, it would be easy to fill many pages with the formulæ of the sub-groups which they form. We shall content ourselves for the present by citing the formulæ of a few sulphur-salts.



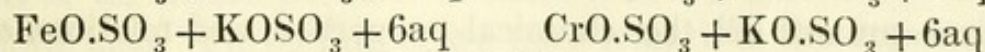
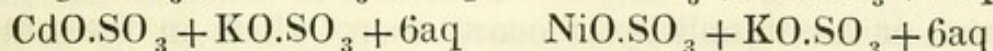
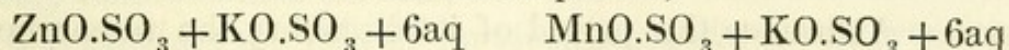
7. The classification of the double salts will obviously depend upon that of the salts of which they are composed, so that we arrange in the same group, all double salts whose proximate constituents belong to the same saline genera. As examples of this mode we may cite the group of salts known as the alums, whose formulæ are



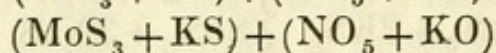
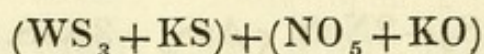
Again, we have an exceedingly well defined group of double salts in certain oxalates, represented by



and in the well known double sulphates,



No double compounds of the other saline sub-groups are known to exist, though there is every probability that double sulphur-salts, chloro-salts and so on, will hereafter be described. We are acquainted with two very remarkable double salts, one of whose constituents is an oxy-salt and the other a sulphur-salt, they are represented by



8. The principles which we have laid down for the classification of single and double salts, apply also to all compounds consisting of three or more oxides, sulphides, chlorides, &c. as well to those which consist of oxides united to chlorides, iodides or other amphides. Under this last head all hydrated salts ought in strictness to be included, together with hydrated amphides, in which the water appears to play a different part from that either of an acid or a base. The same remark applies to those compounds which contain excess of oxide, chloride or amphide in general, beyond and above what is necessary to constitute a neutral salt with the particular acid or base in the compounds. The oxides of zinc, copper and lead, and the proto-chloride of mercury are peculiarly apt to form compounds of this character, and the compounds thus formed we regard as precisely analogous to ordinary hydrates.

To finish the task which we imposed upon ourselves in the commencement of our essay, it remains for us to consider briefly the analogies which subsist between simple and compound bodies.

The discovery of Cyanogen, by Gay-Lussac, furnished the first instance of a compound body which in all its chemical relations bore the most exact analogy to an elementary substance. And since the period of its discovery the researches of chemists have brought to light many other substances of greater or less simplicity of constitution, which in the same manner present all the chemical properties and relations of true elements. It becomes then to us a matter of some importance to determine the principles upon which these bodies are to be classified and arranged according to the principles of a natural system, since it is clear that they must occupy, in any classification, a position essentially different from that of an ordinary compound of two or more elements. If we consider for a moment the properties of these compound elements, if, without an Hibernicism, we may use such an expression,

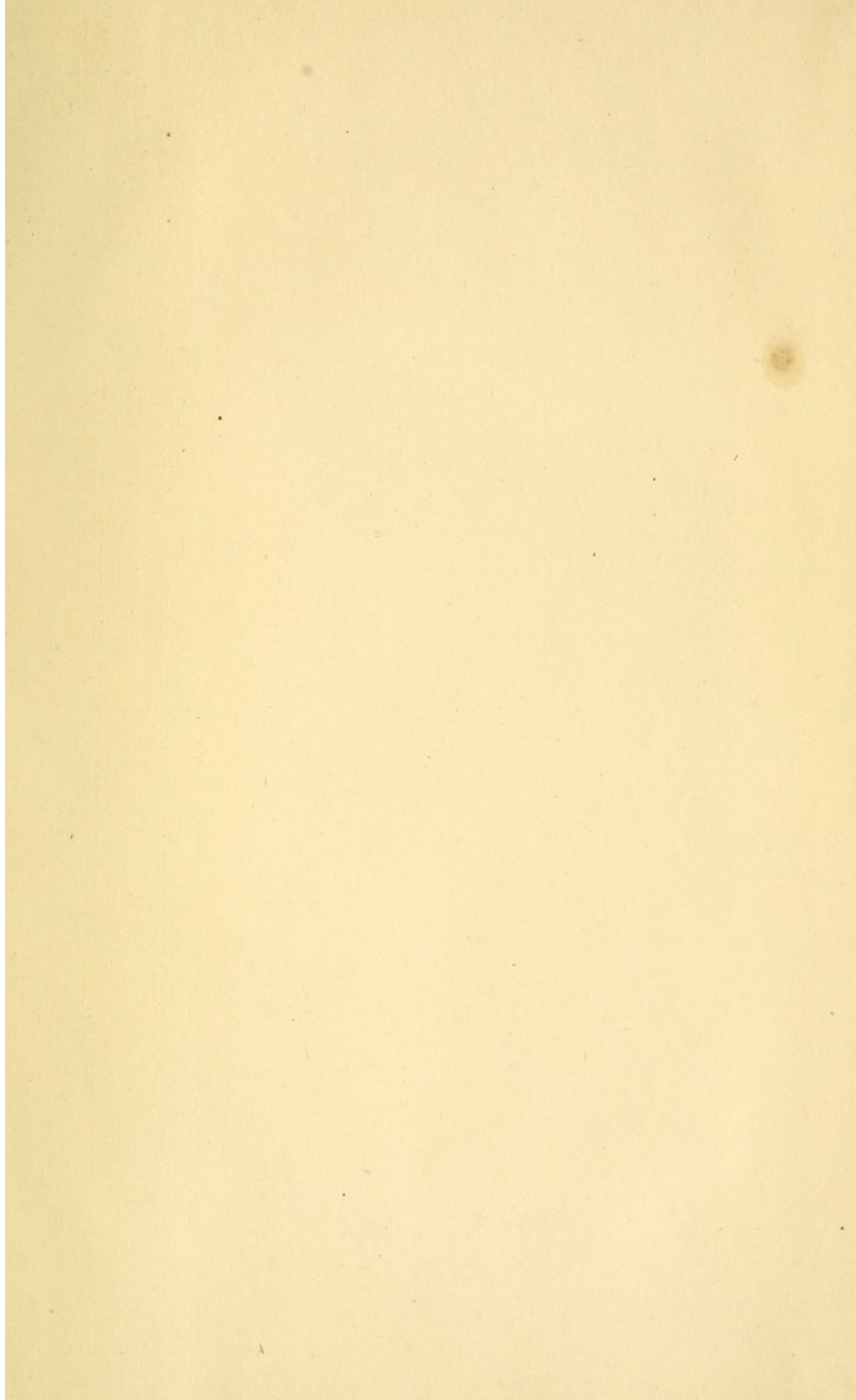
we shall find that, for the purposes of classification, they may be divided into two classes, depending upon their analogies with the amphigen group of our division, or with the non-amphigen groups. Every compound radical is either electro-negative or electro-positive, chlorous or zincous, an analogue of zinc, or a former of acids and bases like oxygen and chlorine. As a chlorous radical we may cite cyanogen; as a zincous radical, ammonium, and as a binary compound of a chlorous with a zincous compound radical exactly analogous to chloride of potassium we may cite cyanide of ammonium. Show us a metallic chloride of a given molecular type and we will produce a corresponding cyanide. Show us a salt of potassium and we will place by its side a similar and even an isomorphous salt of ammonium. It is upon these analogies then that we base our classification of compound radicals. Those which like oxygen or chlorine are capable of forming acid or basic compounds with other radicals, we associate in the same class with oxygen and chlorine, while those on the contrary, which are most distinctly acidifiable or basifiable like metals, we associate either in groups by themselves, according to their analogies with each other, or in the same groups with the simple substances which they may most strongly resemble. It is of course to be constantly borne in mind that compounds like simple radicals are always *relatively* chlorous and zincous, and that the same substance may at one time act the part of an electro-negative or chlorous radical, like chlorine in a metallic chloride, and at another time that of an electro-positive or zincous radical, like chlorine in chloric acid. Furthermore, we may remark in this connexion, that the position of an element when acting electro-negatively may be very different from the position which the same element occupies when acting electro-positively or zincously. For example, electro-negative chlorine is associated by the strongest analogies with oxygen, sulphur, &c. while electro-positive or zincous chlorine is isomorphous in combination

with two equivalents of manganese (or sulphur, though this last is rather inferred than demonstrated.)

Again, chlorous sulphur is analogous to oxygen and the other bodies of the amphigen group, whereas zincous sulphur, as in sulphuric acid, is isomorphous with the elements belonging to the fourth or manganese group, one equivalent replacing one equivalent of metal. Thus the chlorates and perchlorates are isomorphous with the corresponding hypo-manganates and hyper-manganates $\text{ClO}_5 + \text{RO}$ with $\text{Mn}_2\text{O}_5 + \text{RO}$ $\text{ClO}_7 + \text{RO}$ with $\text{Mn}_2\text{O}_7 + \text{RO}$, while the sulphates and seleniates are isomorphous with the manganates and chromates, $\text{SO}_3 + \text{RO}$ and $\text{SeO}_3 + \text{RO}$ with $\text{MnO}_3 + \text{RO}$ and $\text{CrO}_3 + \text{RO}$. The relative states in which bodies exist in combination have not sufficiently attracted the attention of chemists, and it is possible that it is in these conditions that we are to look for the explanation of many phenomena which are at present involved in obscurity.

Thus then, briefly and imperfectly, we have traced through the different elementary bodies the prevalence of the law of grades. We have endeavoured to show that the chemical properties and relations of all substances differ only in degree, and that they are therefore associated together in natural families or groups according to the different degrees of analogies which subsist between them. We have already stated that it is to Graham we owe the first suggestion of a natural system of classification. We regard that idea as one of the most important in the whole history of chemical science, and as likely to lead us to deeper and clearer views upon almost every point in theoretic chemistry, than we have yet been able to attain. A just and comprehensive system of classification has ever been a most powerful instrument in the advancement of a science. As our knowledge advances, many changes will be made in the groups of elements at present adopted as primary, many chasms will be filled up, many new points of analogy discovered, many superficial resemblances detected and exposed, but the principles and the main features of the natural system of arrangement will, we most firmly believe,

remain unchanged. And as with every new discovery, we obtain a farther and clearer insight into the mysteries of nature, we believe that the law of grades will become more and more apparent, till at last it shall be acknowledged that in the Inorganic as well as in the Organic kingdoms, *Natura non facit saltum*.



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