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*ADDRESS OF THE PRESIDENT BEFORE THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.**

THE time-honored custom of our Association makes it incumbent upon the retiring President to deliver an address upon some subject connected, if possible, with his own work, and not purely elementary or historical, but with at least some fresh ideas and some new facts. The task is a difficult one for a chemist, for there is perhaps no branch of science in which, of late years, there has been so much mental activity, and it is hard to find any subject which has not been worn threadbare in discussion.

Trusting to your indulgence, I will here present some theoretical points connected in part with my own work, and will treat them as briefly as the nature of the subjects will permit.

All chemists are familiar with the terms atom and molecule. The use of these two words, with a clear conception of their meaning, forms an era in the history of the science. Our modern chemistry is built up of atoms and molecules, as we now define them. Our modern physics deals for the most part and, as I think, too exclusively with atoms, except, perhaps, in the case of what we now term physical chemistry, the new branch of science, which makes it difficult for us to determine where chemistry

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*Delivered before the Boston meeting, August 22, 1898.

leaves off and where physics begins. The old controversy between the advocates of the continuity and those of the discontinuity of matter is not dead, but only sleeps.

It must be admitted that the conception of the atom, as at present received, is not without serious objections, and probably many accept it as presenting fewer difficulties than the theory of continuity. I venture to suggest that the idea of a material limit, like that of space or quantity in mathematics, avoids at least some difficulties, so that we may define an atom as a limit to which we approach as we subdivide a given mass of any element, having reference to properties alone. Or, taking a somewhat different mathematical conception, we may consider atoms as material differentials of which the general integrals which we term masses are made up, and in this way we may connect purely material with purely mathematical conceptions. The conception of a limit or of a differential avoids all hypotheses as regards form as well as regards magnitude, and retains only ideas of mass and kind. Conversely, I doubt whether, for the purpose of instruction in the calculus, any purely mathematical conception of limits or of differentials and integrals gives as clear an idea of these as does the comparison with physical or chemical atoms and their aggregates.

As all chemists know, we owe to Dalton the first clear conception of the chemical atom as distinguished from the atoms of Leucippus and Democritus; to Frankland the conception of valence which shows us what combinations of atoms can exist consistently with the number of units of affinity possessed by each individual atom, or, in other words, in what manner groups of atoms can form systems which are in stable equilibrium. This conception includes that of the chemistry of space, now so much employed in organic chemistry, as well as that of the motions of atoms within the molecule, as yet almost without supporters. To the conception of a definite number of units of affinity recent chemistry has added that of direction of action, statical according to one school of chemists, dynamical according to another.

Within a comparatively short time attention has been directed to a large class of compounds exhibiting very interesting properties and forming peculiar series, some of which, at least, are made up of homologous terms. This group has been called complex-inorganic, because many of its members form highly complex molecules of which no analogues are known.

I may here remark that Ostwald uses the term 'complex' to denote only those molecules or groups of associated atoms which are unitary and do not belong to the class of double salts. I have not drawn this distinction in the present paper, because it is not that which was originally proposed, and because at present we are not able to separate the two classes from each other, except in a very limited number of cases.

No one class of compounds appears so well adapted to throw light upon the structure and modes of combination of molecules. For this reason I have selected the group as the subject of my address to-day.

In endeavoring to establish a plausible theory of the constitution of the complex-inorganic acids and their salts it will be advantageous to state first succinctly the principal facts to be explained. These, I think, are as follows:

1. The teroxides of molybdenum and tungsten possess, in a remarkable degree, what may be termed a 'cumulative' character, each being capable of forming series of salts which contain a very large relative number of molecules of the teroxide. In this respect they stand alone, so far at least as our present knowledge extends. Certain other oxides share in this peculiarity to a

much less degree, as, for example, chromic and perhaps uranic oxides.

I will cite, in the first place, the series of metatungstates, the existence of which has, I believe, been fully established, partly by the researches of other chemists and partly by those made in my own laboratory.

The first term in the series has the general formula $RO.4WO_3$; the highest appears to be represented by the formula $11RO.24WO_3$. These, with the intermediate compounds, form a series of homologous terms, the common difference being $RO.2WO_3$.

Molybdenum forms a similar, but, in the present state of our knowledge, not so fully represented series. Moreover, in this case, it seems necessary to assume that certain metamolybdates contain a greater or less number of molecules of water as base, either partly or wholly replacing fixed oxides. In my first paper I have discussed this subject, and may here refer to that paper for necessary details. A revision of the composition of the alkaline molybdates is much to be desired, taking specially into account the number of molecules of water retained at high temperatures.

I may here remark that my views in regard to the existence of special classes of metatungstates and metamolybdates have not only not found acceptance with other chemists, but, so far as I know, have never even attracted attention

2. Two different metatungstates may unite to form a double salt, as, for instance,

$$12WO_3.5MO + 10WO_3.4MO + 66H_2O$$
$$12WO_3.5Na_2O + 10WO_3.4Na_2O + 51H_2O.$$

Such compounds, however, are not numerous, and it is possible to explain their structure in other ways. Similar molybdates have not been observed, except in cases in which other oxides, as, for instance, platinic oxide, are present.

3. Metatungstates and metamolybdates may react with a great variety of other salts to form complex salts in which a relatively very large number of molecules of tungstic or molybdic oxides appear, as compared with the number of molecules of the combined salt or oxide.

4. Metatungstates or metamolybdates may unite with complex salts containing tungstic or molybdic oxides, as, for example,

$$10WO_3PtO_24Na_2O + 2\{10WO_34Na_2O\} + 72H_2O.$$

5. Complex acids in the molecule which is united with the tungstic or molybdic oxide appear not to lose their special characters and, in many cases, though not in all, to retain their basicity. Thus in the phospho-tungstate $12WO_3PO_4H_3$ the phosphoric acid is still ortho-phosphoric acid. Two different oxides, acids or salts may unite with tungstic or molybdic oxide, each retaining it own character. I will cite only the phosphoroso-phospho tungstate.

$$24WO_32PO_3H_3P_2O_55K_2O + 13H_2O$$

and the arsenoso-phospho-tungstate

$$32WO_3.14As_2O_3.3P_2O_510K_2O + 28H_2O.$$

Classes of salts have been described in which ortho-phosphoric, hypo-phosphorous, phosphorous, pyro-phosphoric, mono-metaphosphoric and hexa-metaphosphoric molecules appear as such.

The first of the formulas above given may be written

$$22WO_3P_2O_52K_2O.H_2O + 12\,WO_3.2POK_3 + 16\,H_2O$$

and will represent a quadruple salt if each term is to be considered as representing a double salt.

6. In the great majority of cases the number of molecules of water in the meta-salts as well as in their derivatives is extraordinarily large, but in the present state of our knowledge we are unable to distinguish with certainty between water of constitution and water of crystallization.

In considering the theory of the complex inorganic acids it will be most advantageous to begin with the group of silico-tungstates discovered by Marignac. Of these there are four classes, two of which are isomeric. We may write the general formulas of the neutral salts as follows, omitting water of crystallization :

$$10\ WO_3.SiO_2.4RO \qquad 10\ WO_3.SiO_2.2RO.2H_2O$$
$$11\ WO_3.SiO_3.4\ RO$$
$$\left\{\begin{array}{l} 12\ WO_3.SiO_2.4RO \quad 12\ WO_3.SiO_2 2RO.2H_2O \\ 12\ WO_3.SiO_2.4\ RO \end{array}\right.$$

It is, of course, possible that the second group, containing eleven molecules of tungstic oxide, may have twice the molecular mass given, so that the general formula is:

$$12\ WO_3.SiO_2.4RO+10\ WO_3.SiO_2 4RO$$

The potassic salt, which is the only one described by Marignac, will then be the analogue of the double sodium and zinc metatungstate, which I have described, and which has, at least probably, the formula:

$$12\ WO_3.5Na_2O+10WO_3 4ZnO$$

Taking now the first series or group, the general term may be written in one of several ways, as, for example :

(1) $10WO_3.SiO_2(RO)_4$
(2) $10WO_3.RO+SiO_2(RO)_3$
(3) $10WO_3 2RO+SiO_2(RO)_2$
(4) $10WO_3 3RO+SiO_2 RO$
(5) $10WO_3 4RO+SiO_2$

Formulas (1) and (2) appear to be excluded by the fact that silicates of the forms $SiO_2(RO)_4$ and $SiO_2(RO)_3$ are not known to exist, the only forms of silicic acid occurring in silicates containing a single base, in other words, in single as distinguished from double salts, being metasilicic acid SiO_3H_2 and ortho-silicic acid SiO_4H_4 or SiO_2H_2O and $SiO_2 2H_2O$ or corresponding salts. On the other hand, formulas (3) and (4) are admissible so far as the silica is concerned, but considered as double salts they require us to assume the existence of 10 $WO_3 2RO$ and 10 $WO_3 3RO$, which are not known to exist. Formula (5) is also admissible, if we suppose that a molecule of water is present, and thus we have 10 $WO_3.4RO+SiO_2OH_2$.

Marignac considered all the acids of this series as quadribasic and consequently that two molecules of basic water were present in each of a number of well defined salts.

From the above it appears difficult to explain the constitution of the various silico-tungstates and tungsto-silicates if we consider them as simply double salts. We must assume either that tungstates not known to exist or that silicates which have no analogues or that both these classes enter together into the structure of the complex molecules.

We get no assistance from a consideration of the mode of preparation of the complex salts in question. Marignac obtained them by boiling gelatinous silica with metatungstates. Gelatinous silica has no definite constitution, but appears to be simply a mixture of two or more forms of silicic acid. It has not been shown, I believe, that soluble alkaline silicates dissolve tungstic oxide on boiling, but Parmentier found that silico-molybdates are formed by the action of alkaline silicates upon alkaline molybdates in presence of silicic acid, and Pechard has shown that a silico-molybdate of the twelve molecule series is formed by the action of fluosilicic acid upon the 14:6 metamolybdate of ammonium.

The same reasoning applies to the silico-tungstates and tungsto-silicates, which contain twelve molecules of tungstic oxide, since the last named classes of acids also unite with four molecules of base.

In this connection three remarkable double salts deserve notice. These have respectively the formulas:

$36WO_3.3SiO_2.2Al_2O_3 + 93H_2O$ and $+ 81H_2O$
$36WO_33SiO_2.2Al_2O_3(NH_4)_2O + 75H_2O$
$36WO_3.3SiO_2.2MO_5.8Na_2O + 45H_2O.$

These salts may all be considered as containing three molecules of the complex:

$$12WO_3.SiO_2.$$

The two first may be, respectively:

$2(Al_2O_33H_2O) + 3(WO_3SiO_24H_2O) + 75H_2O$
$2(Al_2O.3H_2O)$
$+ 2(12WO_3SiO_2.3(NH_4)_2OH_2O + 63H_2O$

and the third:

$2(N_2O_5Na_2O) + 3(12WO_3SiO_22Na_2O2H_2O)$
$+ 39H_2O.$

The following also deserve notice in the same connection:

$12WO_3SiO_23K_2O.H_2O$
$+ 12WO_3SiO_2.2K_2O_32H_2O + 26H_2O.$
$12WO_3SiO_2.3CaO.H_2O$
$+ 12WO_3SiO_2.2CaO.2H_2O + 46H_2O.$

The simplest view which can be taken of all these compounds is that they contain the complex $12WO_3.Sio_2.4RO$ and that they are double and not quadruple salts or acids. And it seems to me that the weight of evidence is in favor of the view that the complex $WO_3SiO_2.4RO$ or $10WO_3SiO_2.4RO$ is single or unitary and not a double salt of a tungstate and silicate.

Marignac did not attempt to explain the isomerism of silico-tungstic and tungsto-silicic acids, and the problem is one of much interest, since there are no allotropic modifications of tungsten or silicon.

To obtain a further insight into the constitution of the simpler complex acids we may, with advantage, also consider the cases of the phosphotungstates and phosphomolybdates. As normal we may take the acids $12WO_3.PO_4H_3$ or $12MoO_3.PO_4H_3$. These correspond to the twelve molecule silico tungstates or tungsto-silicates of Marignac, and the reasoning applied to these cases will apply also to the phosphotungstates and phosphomolybdates. Only in these last the number of known compounds is much greater, acids in which the proportion of tungstic or molybdic oxide to phosphoric oxide is as 24:1, 22:1, 20:1, 18:1, 16:1, 5:1, being known in their corresponding salts. Besides these we have arsenic compounds in which the ratio of tungstic or molybdic oxide to arsenic oxide is as 6:1 and 7:1, as well as double salts in the ordinary acceptation of the term. Instances of these last are:

(1) $22MoO_3.P_2O_5.3K_2O$
$+ 22MoO_3.P_2O_5.2K_2O.H_2O + 21\ H_2O.$
(2) $2(20MoO_3.P_2O_5.3(NH_4)20)$
$+ 20MoO_3.P_2O_5.2(NH_4)_2O.H_2O + 11\ H_2O.$
(3) $24MoO_3P_2O_5.3(NH_4)_2O$
$+ (24MoO_3.P_2O_5.2(NH_4)_2O.H_2O + 16\ H_2O.$

Upon any other than the view which I have taken the phosphotungstates and phosphomolybdates of the types $nWO_3P_2O_56RO$ and $nMo_3.P_2O_56RO$ are salts *sui generis* analogous to metatungstates and metamolybdates. The compounds expressed by these last formulas are quaternary.

We may compare these salts (1), (2) and (3) with the double tungstate

$$12\ WO_35Na_2O + 10\ WO_3.4Na_2O + 51\ aq.$$

They behave like salts of meta-tungstates or meta-molybdates which have taken into their structure molecules of phosphoric or arsenic oxides without materially changing their general character. The precise mode of combination of the tungstic and molybdic molecular masses with silica, phosphoric or arsenic oxides is not at present known, but it is not difficult to show that the units of affinity of all the elements present may be accounted for and illustrated by structural diagrams. In like manner, the condensation of n molecules of tungstic or molybdic teroxide is easily explained, the number of unsaturated or residual units of affinity being for all values of n equal to 2, as in the case of water.[*]

The study of the complex acids which contain ortho-phosphoric acid as such naturally led to that of complex acids containing other acids of phosphorus. The greater number, or at least the more important, of these have been shown to give well-defined complex acids, and in all cases appeared to contain the phosphorus compound in the modification in which it existed before the combination with tungstic or molybdic oxide. Since this work was completed several new acids containing phosphorus have been discovered, more especially the so-called hypo-phosphoric acid, and it is to be hoped that these also will be studied from the same point of view. I shall ask attention to the compounds now known. The only pyrophospho-tungstates yet observed belong to the general types for the acids

$$(22WO_3.9P_2O_7H_4)\ 2RO.$$

and for the salts

$$(22WO_3.9P_2O_7R_2.)\ 2RO.$$

The salts containing molybdic teroxide differ from the above and belong to different types. All those which were examined contained manganous oxide and all contained but two molecules of pyrophosphoric acid or corresponding pyrophosphates in place of nine. It is not easy to see how the presence of manganous oxide as base can affect the formation of such salts, but the analyses of a pyrophospho-tungstate containing six molecules of manganous oxide correspond very closely to a formula embraced under the type

$$14WO_3.6RO + P_2O_7R'_4.$$

so that, so far as the empirical constitution is concerned, the salt may be regarded as double and as containing two salts belonging to well known types. In the present state of our knowledge it seems more probable that the pyrophospho-tungstates and pyrophospho-molybdates are double salts belonging to the second class of complex inorganic salts. The solutions of the alkaline salts give, with solutions of the heavy metals, precipitates which contain only pyrophosphoric acid and neither tungsten nor molybdenum. On the other hand, it is well worthy of notice that the group

$$9(P_2O_7R_4)$$

is capable of existing independently of tungstic oxide. Wallroth has shown that we have salts of the type

$$(P_2O_7)_9R''_{10}Ne_{16}.$$

Of the other modifications of phosphoric acid I shall notice only the mono-metaphosphates and the hexa-metaphosphates. In the case of the former the type of the tungsten compounds is:

$$(mWO_3.2PO_3R)pR'O.$$

As in the case of the pyrophospho-tungstates we have here to distinguish an internal and an external basicity, the group $(mWO_3.2PO_3R)$ standing in the relation of a complex oxide to the external group $pR'O$. For the mono-meta-phosphomolybdates the type is different:

$$(m'MoO_34PO_3R)p'R'O$$

and, of course, other types are possible. So far as we can now judge the salts containing mono-meta-phosphoric acid belong to the first group like phosphotungstates and phosphomolybdates of the type

$$12WO_3.PO_4R_3 \text{ and } 12MoO_3PO_4R_3.$$

They give no reactions characteristic of their constituents, but the precipitates which they form with metallic salts have the oily or pasty character of the salts of metaphosphoric acid.

The only hexa-metaphosphomolybdate examined has the formula

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[*] See *American Journal of Science and Arts*, Vol. XLIV., November, 1867.

$$(14MoO_3.6PO_3Ba_3)BaO + 55\ H_2O.$$

and we may safely infer that the type is

$$(mMoO_3.6PO_3R_3)pRO,$$

there being an internal and external basicity, as in the cases above noted.

It is worthy of note that in all the known acids containing phosphorus in some oxidized form other than orthophosphoric acid the number of molecules of the acid united to tungstic or molybdic oxide is greater than in the ortho-phosphotungstates or ortho-phosphomolybdates containing an equal number of molecules of tungstic or molybdic oxides.

Two classes of phosphorus compounds remain to be considered—those which contain phosphorous and those which contain hypophosphorous acid or corresponding salts. Chemists are not wholly agreed as to the rational constitution of either of these acids, but it is perhaps more probable that the phosphorous molecule is represented by the formula

$$\{H.PO(OH)_2\}$$

and the hypophosphorous molecule by the formula

$$\{H_2PO.OH\}.$$

The typical formula for salts containing the former is

$$mWO_3.n\{H.PO(OR)_2pR'O$$

or $$m'MoO_3.n'\{H.PO(OR)_2p'R'O.$$

and for those which contain the hypo-phosphorous molecule

$$mWO_3n\{H_2PO.OR\}pRO$$
$$m'MoO_3n'\{H_2PO.OR\}p'R'O$$

Both groups of salts appear to belong to the first class of complex acids or salts. It is worthy of notice that the phosphorous and hypo-phosphorous salts do not reduce copper from its solutions even on boiling, and they can, therefore, hardly be supposed to be simply double salts in the ordinary acceptation of the term.

We owe to Blomstrand the discovery of a specially remarkable and interesting class of complex acids, the molybdo-periodates or, in the notation which is more commonly used, periodo-molybdates. The acid of this series has the formula:

$$12MoO_3.I_2O_7.5H_2O.$$

and is the analogue of phosphomolybdic acid.

$$24MoO_3.P_2O_5.3H_2O.$$

The salts of this series are 5-basic, but, as in the case of metatungstates and metamolybdates, these are composed of two or more normal salts. The best defined of these has the formula:

$$(12MoO_3.I_2O_7.5K_2O)$$
$$+ (12MoO_3I_2O_7.2K_2O.3H_2O) + 30\ H_2O.$$

which we may compare with

$$(24MoO_3.P_2O_53(NH_4)_2O)$$
$$+ (24MoO_3.P_2O_5.2(NH_4)_2O.H_2O)16\ H_2O.$$

In the complex acids, of which the present paper treats, we may consider the teroxides of tungsten and molybdenum as the determinants. Oxides, of which SiO_2, P_2O, R_2O_3 and I_2O_7 may serve as types, may be regarded as sub-determinants. The chemical potential of the compound will, of course, be a function of the chemical potentials of both determinants and sub-determinants. Protoxides appear not to form sub-determinants, but in all cases to act simply as bases. One of the difficulties of our subject consists in determining how far the sub-determinants proper may act as bases, and especially whether they are not sometimes partly bases and partly sub-determinants in the same salt.

In my published paper I have made two assumptions as regards the rôle of vanadic pentoxide in the vanadio-tungstates and vanadio-molybdates.

The first is that $V_2O_2.O_3$ may replace WO_3 so that chemically

$$mWO_3 + n(V_2O_2)O_3$$

may act as a whole; the second that V_2O_5 may form combinations with a number of molecules of tungstic or molybdic teroxide analogous to phosphotungstates or phosphomolybdates. These assumptions, taken separately or together as the case may require, in many cases at least reduce complex to simple formulas perfectly comparable to those of salts containing phosphoric or arsenic pentoxide. Thus we have

$$5WO_3.V_2O_5.4(NH_4)_2O.2H_2O + 11H_2O.$$
$$5MoO_3.V_2O_5.3(NH_4)_2O.3H_2O + 4H_2O \text{ and}$$
$$8MoO_3.V_2O_5.3BaO + 8MoO_3.2BaO.H_2O.$$

In addition I have described two vanadiotungstic acids having respectively the formulas:

$$10WO_3.V_2O_5.6H_2O + 16\ H_2O.$$
$$18WO_3V_2O_5.6H_2O + 30\ H_2O.$$

The existence of these compounds has been denied,* but I see no sufficient reason for rejecting the formulas, which at least closely correspond to the analyses. The same remark applies to the acid

$$20V_2O_5.P_2O_5.6H_2O + 53\ H_2O.$$

or

$$20V_2O_2O_3.P_2O_5.6H_2O + 53\ H_2O.$$

which I would compare with

$$20WO_3.P_2O_5.6H_2O.$$

It must be admitted, however, that in view of the extraordinary number and variety of the combinations of vanadic pentoxide with bases it cannot be denied that there are very numerous compounds of this oxide with the teroxides of tungsten and molybdenum, which, in the present state of our knowledge, must be classed as double salts. The empirical composition of these salts may be expressed by the general formula:

$$mWO_3.nV_2O_5.pRO$$

or

$$m'Mo_3n'V_2O_5p'RO.$$

in which m, m′ represent respectively the number of molecules of tungsten or molybdenum and n, n′, p, p′ are whole numbers. Friedheim assumes that in many of these compounds vanadic pentoxide acts as a base and that in others mixtures of isomorphous salts are present. The pentoxide dissolves readily in the stronger acids, as, for instance, in sulphuric and phosphoric acids, but I am not aware that well defined crystalline salts of this oxide have been obtained. There are also, I believe, no known instances of isomorphism between tungstic and vanadic or molybdic and vanadic oxides. In spite, therefore, of all that has been done, it seems necessary to admit that our knowledge of the vanadio-tungstates and vanadiomolybdates is still very imperfect, but this remark applies also to the very large group of alkaline vanadates.* Of course, the theory that in the salts in question we are dealing, chiefly at least, with double salts is that which would naturally present itself first, but we meet with the difficulty that the constituents of these double salts are themselves double salts, so that we must deal in fact with triple and quadruple salts.

In my view the acids or salts which are usually termed complex may be divided into two classes.

Class first embraces those in which the union of the determinant and sub-determinant is so complete that the special characters of the constituents are nearly or wholly lost. The salts of this class are not decomposed by solution. They may be compared to certain so-called double cyanides, as, for example, to ferrocyanides and cobalticyanides. The acids $12\ WO_3.PO_4H_3$ and $12\ MoO_3.PO_4H_3$ are examples.

Class second embraces double salts proper which are decomposed by solution alone and which contain two different constituents. Salts of this class are very numerous, and there are probably various sub-classes.

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*See Friedheim. Berichte, Band XXIII., p. 1505 and 1530 (and Rosenheim Dissertation, Berlin, 1888); Zeitschrift für amorgan. Chemie, Band V., p. 437; Berichte, Band 24, p. 1173.

*See Proceedings of Am. Acad., Vol. XVIII., p. 74.

In the present state of our knowledge it is not possible for us to assign to more than a few acids the classes to which they belong, and a vast field of chemico-physical work is open to the investigation of this subject alone.

We have also to determine by methods now well known to chemists the molecular masses of metatungstates and metamolybdates and of the complex inorganic acids, which may be considered as derived from, or at least as definitely related to them. Certain double salts appear to be composed of metatungstates or metamolybdates united to salts containing subdeterminants, as, for instance, and more especially, platinic oxide. I may, for the sake of clearness, refer to such formulas as

$$10\,WO_3.4Na_2O + 10\,WO_3.PtO_2.5Na_2O + 58aq.$$

and

$$4\{12MoO_3.2K_2O.3H_2O\} + \{12MoO_3.PtO_2.2K_2O.4H_2O\} + 24aq.$$

These salts appear not to be decomposed by water and to belong therefore to class first.

The compounds of arsenic oxide with tungstic and molybdic oxides closely resemble those of phosphoric oxide and do not now require special notice as regards their structure and properties, nor as to the question of their position as unitary or double salts.

On the other hand, the salts which contain arsenious oxide present some special points of interest, since this oxide exhibits distinct basic and, in its salts, distinct acid properties. The general formulas for this class of compounds, so far as they have been studied, are

$$mWO_3.nAs_2O_3.pRO \text{and } m'MoO_3n'As_2O_3.p'RO$$

As characteristic salts we may take the arsenoso-molybdates

$$6MoO_3.3As_2O_3.2RO$$

of which four have been obtained in fine crystals.

The copper and nickel salts of this type have a fine green color and, therefore, contain the two metals as ions, at least in part. It is, therefore, most probable that the salts are unitary. This view is supported by the fact that the alkaline salts from which the salts of manganese, copper, zinc and nickel are obtained by double decomposition give reactions which are different from those of the constituent molybdic and arsenious oxides. The same statement applies to other known arsenoso-molybdates and to arsenoso-tungstates.

I pass over without notice a number of interesting salts, some of which contain for a single determinant at least three different sub-determinants, as, for example, phosphoric and vanadic pentoxides and vanadic dioxide. We are only at the beginning of our knowledge of these compounds. From their extreme complexity it would seem most probable that they belong to the second class and are in some cases double, triple or quadruple salts, of which possibly the components may belong to the first class. Long and laborious investigations are required, sure to be rewarded by an abundant harvest of new facts, of little or no practical value perhaps, but to be looked at from the higher point of view of pure abstract knowledge.

The term 'complex inorganic' was at first intended to embrace all the compounds containing a relatively large number of molecules of tungstic and molybdic oxides as determinants, beginning with the silicotungstates of Marignac. Hittorf, in 1859, appears to have first drawn the distinction between double salts which are decomposed by solution and those which are stable under the same circumstances. Finally, Ostwald proposed to restrict the term 'complex' to the salts which are not decomposed by solution and which gave none of the chemical reactions of the constituents.

Of these two classes it is difficult to say which is the more interesting and theoretically important. The salts of the first class are comparatively new to chemists, and, in spite of all which has been done, offer a very wide field for investigation. Those of the second class present new species of double and even of triple and quadruple salts. It will first be necessary to study the whole subject by physical as well as by the purely chemical methods which all chemists have hitherto employed, so as to define as distinctly as possible the limit, if there be one, which separates the two classes from each other. I make the point that all known methods of distinguishing double from unitary salts should be employed in each case, as I believe it has not yet been satisfactorily shown that all these methods give coincident results. It seems also possible that there may exist between the two classes given a third class, the salts belonging to which exhibit intermediate properties. In chemistry, as in other branches of science, sharply defined boundaries between groups are the exception. I am not aware that the chief methods of distinguishing between single and double salts have been brought together for reference, and perhaps the following list may be convenient:

1. Purely chemical or reaction tests.
2. Decomposition by solution alone.
3. Physical methods.
   a. Determination of the electric conducting power of dilute solutions.
   b. Determination of the ions by electrolysis and by spectroscopic observations.
   c. Observation of the change of temperature in the formation of the complex salt. Heat is evolved in the formation of a complex salt from unitary molecules; none in the formation of a double salt. The formation of a complex salt, therefore, is accompanied by a loss of energy.

Other methods have been given, but the above mentioned will suffice for most purposes.

In the brief and elementary sketch which I have given to-day of two large and important classes of salts I have avoided the use of the so-called structural, or, as they should be termed, valence formulas. That such formulas are often useful, if only as checks upon purely speculative work, cannot be doubted. But it seems to me that the time has come for wider and more general conceptions of the chemical action between masses, subject perhaps to the fundamental idea of valence and yet not too dependent upon this idea as at present received. In a paper published long since, an attempt was made to extend the atomistic conception and to maintain the theory that the action of one complex mass upon another is determined by the residual unsaturated units of affinity present, without reference to the number of units due to each atomic mass. I venture now to suggest that, in addition to its valence, each atom and each molecule possesses a special chemical potential, not necessarily a function of its valence. The expression 'chemical potential' is not wholly new, but I think the conception has never been clearly defined. I would now define it as bearing the same relation to chemical action which the electric potential bears to electrical action, the two potentials being mutually convertible, all chemical compounds having residual affinities or potentials besides the valencies. If we suppose that the atoms within the molecule are in motion, such motion will be independent of the valences and the molecule will have a certain amount of free kinetic energy convertible into chemical electrical energy or into heat.

In inorganic chemistry four great problems now present themselves for solution. These are:

The existence and chemical relations of the gaseous elements, of which five are known to exist in the atmosphere. The separation of the elements forming the rare earths, by systematic processes and the determination of their positions in the periodic series ; the thorough and, so far as possible, exhaustive study of the complex and double salts and, finally, the determination of the atomic masses of the elements with all the precision of which the subject admits, and in the spirit of Stas, of Richards and of Morley.

Wolcott Gibbs.

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*A HALF-CENTURY OF EVOLUTION, WITH SPECIAL REFERENCE TO THE EFFECTS OF GEOLOGICAL CHANGES ON ANIMAL LIFE.**

Only a little less than fifty years have passed since the publication of Darwin's Origin of Species, and the general acceptance by naturalists of the theory of descent. Since 1848 the sciences of embryology, cytology and comparative anatomy based on embryology, or, as it is now called, morphology, have been placed on a firm foundation. It is but little over half a century since the uniformitarian views of Lyell were promulgated. The cell doctrine was born in 1839; the view that protoplasm forms the basis of life was generally received forty years since ; fifty years ago the doctrine of the conservation of forces was worked out, and already by this time had the idea of the unity of nature dominated the world of science.

On the fiftieth anniversary, therefore, of our Association, it may not be out of place, during the hour before us, first, briefly to inquire into the present state of evolution and its usefulness to zoologists as a working theory, and then to dwell more at length on the subject of the effect of geological changes on animal life.

The two leading problems which confront us as zoologists are: What is life ? and How did living beings originate? We must leave to coming centuries the solution of the first question, if it can ever be solved ; but we can, as regards the second, congratulate ourselves that, thanks to Lamarck, Darwin and others, in our day and generation, a reasonable and generally accepted solution has been reached.

Time will not allow us to attempt to review the discoveries and opinions which have already been discussed by the founders and leaders of the different schools of evolutionary thought, and which have become the common property of biologists, and are rapidly permeating the world's literature.

It may be observed at the outset that, if there is any single feature which differentiates the second from the first half of this century, it is the general acceptance of the truth of epigenetic evolution as opposed to the preformation or incasement theory, which lingered on and survived until a late date in the first half of the present century.*

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*Address of the Vice-President before Section F.—Zoology—of the American Association for the Advancement of Science, August 22, 1898.

*The theory of incasement (*emboîtment*), propounded by Swammerdam in 1733, was that the form of the larva, pupa and imago of the insects pre-existed in the egg, and even in the ovary, and that the insects in these stages were distinct animals contained one inside the other, like a nest of boxes, or a series of envelopes one within the other ; or, in his own words : "*Animal in animali, seu papilio intra erucam reconditus.*" Réaumur (1734) also believed that the caterpillar contained the form of the chrysalis and butterfly, saying : "Les parties des papillon cachées sous le fourreau de chenille sont d'autant plus faciles à trouver que la transformation est plus proche. Elles y sont neanmoins de tout temps." He also believed in the simultaneous existence of two distinct beings in the insect. "Il serait très curieux de connaître toutes les communications intimes qui sont entre la chenille et le papillon. * * * La chenille hache, broye, digere les aliments qu'elle distribué au papillon ; comme les mères préparent ceux qui sont portés aux fœtus. Notre chenille en un mot est destineé à nourrir et à defendre le papillon qu'elle renferme." (Tome i, 8^{e} Mémoire, p. 363.)

It was not until 1815 that Herold exploded this error, though Kirby and Spence in 1828, in their Introduction to Entomology, combated Herold's views and maintained that Swammerdam was right. As late as 1834, a century after Swammerdam, Lacordaire, in his Introduction à l'Entomologie, declared that 'a caterpillar is not a simple animal, but compound,' and he actually goes so far as to say that 'a