102.6 : 1000 = 9.62 : x or, x = 93.7622 g. of mercuric chloride per liter of solution, and

$$\frac{93.7622}{0.271} = 346.0$$ millimols per liter of solution of mercuric chloride and water at 40°.

SEATTLE, WASHINGTON.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY AND THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL.]

THE ELECTRON CONCEPTION OF VALENCE. VI. INORGANIC COMPOUNDS.

BY J. M. NELSON AND K. GEORGE FALK.

Received October 22, 1914.

In the previous papers of this series,[1] the view that two atoms when combining acquire opposite electric charges was developed and applied to various classes of compounds and reactions.

In this paper, the electron conception of valence will be applied more especially to compounds and reactions of inorganic chemistry. The natural method of studying the present problem is to take the classifications developed by Werner and to consider them from the point of view of the electron conception of valence. It is manifestly impossible in a paper such as this, to take up all the relations Werner has developed. Instead, only some of the more important will be chosen, and the application of the electronic view to these, considered.

In discussing the structures of inorganic compounds, it is useful to consider many of them as tautomeric. The conception of tautomerism has been most useful in organic chemistry, where a number of tautomeric forms of various substances have been isolated and their chemical and physical properties studied. Tautomeric formulas have also been proposed for certain inorganic substances. Recently, Bray and Branch,[2] as well as Lewis,[3] developed valence views from this standpoint in papers entitled "Valence and Tautomerism."

The application of the electron conception of valence to the phenomenon of tautomerism was outlined in previous papers. It was shown that the algebraic sum of the charges on each atom in a substance capable of existing in tautomeric forms remains the same in each of the forms, although the arrangement of the atoms may be different. This may be illustrated by the formulas for hydrocyanic acid, nitrous acid, and ethyl acetoacetate:

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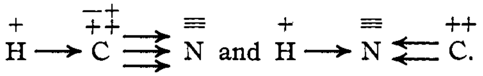
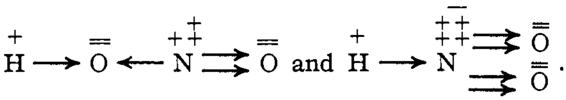
[1] *School of Mines Quarterly*, 30, 179 (1909); THIS JOURNAL, 32, 1637 (1910); 33, 1140 (1911); 35, 1810 (1913); 36, 209 (1914); *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, 6, 212 (1912); *J. prakt. Chem.*, (*N. F.*), 88, 97 (1913); *Proc. Amer. Philosoph. Soc.*, 53, 25 (1914).

[2] THIS JOURNAL, 35, 1440 (1913).

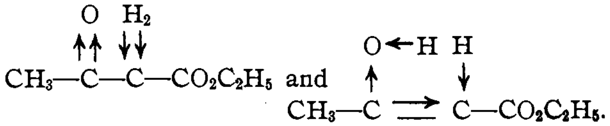
[3] *Ibid.*, 35, 1449 (1913).

Hydrocyanic acid 

$\overset{+}{H} \longrightarrow \overset{\overset{-+}{++}}{C} \Rrightarrow \overset{\equiv}{N}$ and $\overset{+}{H} \longrightarrow \overset{\equiv}{N} \Lleftarrow \overset{++}{C}.$

Nitrous acid 

$\overset{+}{H} \longrightarrow \overset{=}{O} \longleftarrow \overset{\overset{+}{++}}{N} \rightrightarrows \overset{=}{O}$ and $\overset{+}{H} \longrightarrow \overset{\overset{-}{\overset{++}{++}}}{N} \begin{matrix} \rightrightarrows \overset{=}{O} \\ \rightrightarrows \overset{=}{O} \end{matrix}.$

Ethyl acetoacetate 

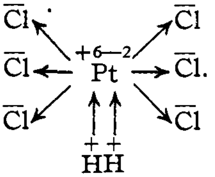
$CH_3\text{—}\overset{\overset{O}{\uparrow\uparrow}}{C}\text{—}\overset{\overset{H_2}{\downarrow\downarrow}}{C}\text{—}CO_2C_2H_5$ and $CH_3\text{—}\overset{\overset{O\leftarrow H}{\uparrow}}{C} \rightleftarrows \overset{\overset{H}{\downarrow}}{C}\text{—}CO_2C_2H_5.$

These formulas show that there is no oxidation or reduction reaction involved in the change of a tautomeric substance from one form to another. This is an important point in the further considerations.

Another fundamental relation is that which was described as onium compound formation and decomposition in a former paper,[1] and which involves the simultaneous loss and gain of a valence electron by one or more atoms of one or more molecules in a reaction. The formation of ammonium chloride from ammonia and hydrochloric acid according to the equation[2] $\overset{\equiv+}{NH_3} + \overset{+-}{HCl} = \overset{\overset{-}{\equiv++-}}{NH_4Cl}$ in which the valence of the nitrogen is —3 in the one case and —4 + 1 = —3 in the other, is a simple example of this.

In beginning the study of inorganic compounds, it is advisable to consider a substance whose structure cannot be questioned. Platinic chloride must undoubtedly be represented by $\overset{\overset{++}{++-}}{PtCl_4}$. To pass from platinic chloride to chloroplatinic acid involves no oxidation or reduction of any of the atoms involved as far as can be told, and the latter may, therefore, be represented by the formula

$$\overset{+}{H_2}\overset{\overset{++}{\overset{++}{=++}}}{Pt}\overset{-}{Cl_6} \quad \text{or}$$



Chloroplatinic acid is a dibasic acid and may, therefore, also be written

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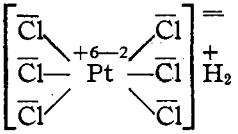
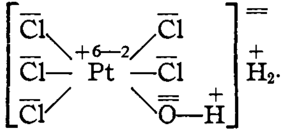
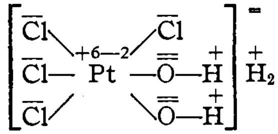
[1] IV paper of this series, This Journal, 35, 1810 (1913).

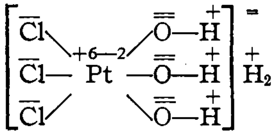
[2] This equation is probably not complete, as the presence of moisture is necessary for the reaction to proceed with finite velocity. It is possible, if the moisture acts purely catalytically, that this reaction would proceed as given although at a much smaller rate. In any event, the equation represents the change in the valence of the nitrogen atom to which it is desired to call attention in this connection.

 to show this ionization. The valence of the platinum, or its state of oxidation, is +6 — 2 = +4 in chloroplatinic acid, just as it is in platinic chloride. The addition of hydrochloric acid to platinic chloride represents an onium compound formation. The negative chlorine combined with the positive platinum is not ionized, but the positive hydrogen combined with the positive platinum is ionized. The various chloroplatinic acids[1] may be considered next. In chloroplatinic acid, $PtCl_4.2HCl$, HCl may be replaced by H_2O. This substance, pentachloroplatinic acid, $PtCl_4.HCl.H_2O$, is also a dibasic acid. Without considering at present the possible mechanism of the reactions involved, but only the final formulas themselves, the structure of pentachloroplatinic acid must be analogous to that of chloroplatinic acid, or H_2O plays a part similar to that played by HCl. The formula for pentachloroplatinic acid must then be represented by 

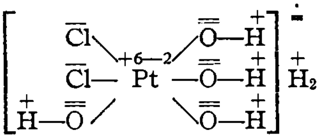
By analogy and in complete accord with the experimental facts, the positively charged hydrogens combined with the positive platinum are ionized, while the negatively charged atoms or groups combined with the positive platinum are not ionized. The other acids of this group given by Werner may be formulated in the same way:



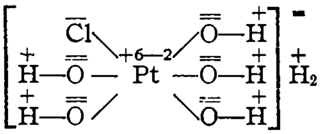
Tetrachloroplatinic acid.



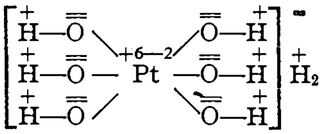
Trichloroplatinic acid (not known).



Dichloroplatinic acid.



Monochloroplatinic acid.



Platinic acid.

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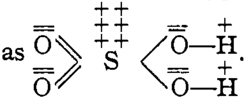
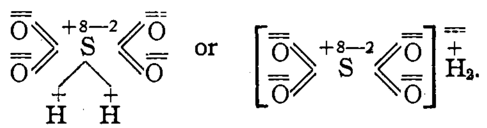
[1] Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," III Edition (1913), pp. 40–1.

The fact that these acids are all dibasic proves that the acidity is not connected with the hydrogen of the hydroxyl groups,[1] and by comparing the whole series from chloroplatinic acid to platinic acid it is evident that the ionizable hydrogens are those combined directly with the positive central atom, platinum in this case. The salts of these acids may be formulated similarly.

Platinum evidently is not capable of taking up in onium combination an unlimited number of positively and negatively charged atoms or groups. The compounds just considered show that the maximum number of positive charges that a platinum atom is able to receive (or negative atoms or groups that it can hold in direct combination) is six.[2] However, in compounds in which this maximum positive valence is shown, the platinum has also two negative electrons or valences with which it holds two positive atoms or groups. While six is the maximum number of positive charges that the platinum atom can hold, it does not in such compounds attain a higher state of oxidation than that represented by four positive charges.

Possibilities of tautomerism exist for these platinum acids but there is at present no experimental evidence that they have been realized. A consideration of these possibilities might obscure and confuse the main points which the discussion of the structures just given, is intended to bring out, so that it will not be given in this connection. Such possibilities will be considered later in connection with other substances.

It will be of interest to take up next a number of acids containing oxygen. Sulfuric acid will be chosen as a typical example. Its structure is formulated ordinarily as . This structure is based upon a number of experimental facts, such as the reactions of organic derivatives of the acid and related compounds, the successive replacement of hydroxyl groups, etc. From the discussion of the platinum acids, it appears to be highly improbable for a substance with this formula to ionize as an acid. If, however, the structure is written in the tautomeric form, this difficulty disappears and sulfuric acid falls in line with the platinum acids. The tautomeric form of sulfuric acid is



The positively charged ionizable hydrogen is in direct combination with the positive sulfur, while the negative oxygen (or hydroxyl in the first

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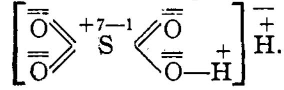
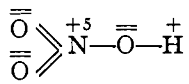
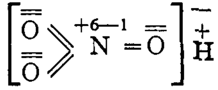
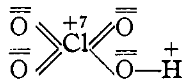
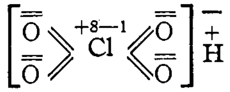
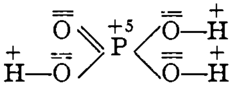
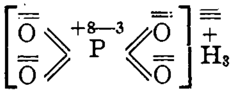
[1] Werner, *Loc. cit.*, p. 32.

[2] The maximum coördination number of Werner, *Loc. cit.*, p. 52.

form) combined with the positive sulfur is not ionized. The state of oxidation of the sulfur atom is the same (+6) in both cases. An equilibrium unquestionably exists between the tautomeric forms of sulfuric acid. An intermediate form in which only one hydrogen is in direct combination with sulfur is possible and undoubtedly exists. Its formula would be  These formulas and the possible equilibria between the different tautomeric forms, together with the view that the hydrogen is ionized only when in direct combination with the central atom carrying a predominatingly positive charge, is suggestive in a number of directions. For instance, the anomalous behavior of strong electrolytes on ionization may, in part, be due to the existence of the tautomeric forms in solution and their different degrees of ionization.

It is evident that all oxygen acids and salts may be considered in the same way. The formulas for some follow:

	Non-ionizable form.	Ionizable form.
Nitric acid		
Perchloric acid		
Phosphoric acid		

The number of oxygen atoms in combination with the central atom depends upon the specific chemical nature of that atom. In general, Werner points out[1] that four or six oxygen atoms held by the central atom represent the two common types of compounds of this nature. Considered from the electronic point of view, the central atom in these two types in the ionizable forms would possess eight or twelve positive charges due to the combination with the negatively charged atoms or groups, while the ionizable positively charged atoms or groups would give the central atoms a certain number of negative charges or corpuscles. The difference between the number of positive and of negative charges of these central atoms represent their state of oxidation. In nitric acid, the state of oxidation of the nitrogen atom is represented by five positive charges; of chlorine in perchloric acid by seven positive charges; of phosphorus in phosphoric acid by five positive charges, etc. With phosphoric acid, other intermediate tautomeric forms are possible and probably exist as indicated with sulfuric acid. Here, as there, the experimentally measured ionization may depend to a great extent upon the equilibria between the

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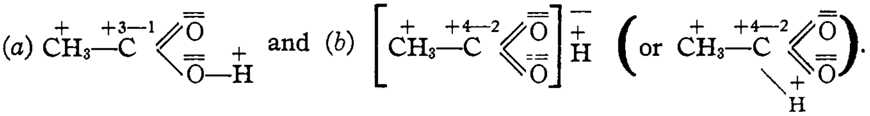
[1] *Loc. cit.*, p. 121.

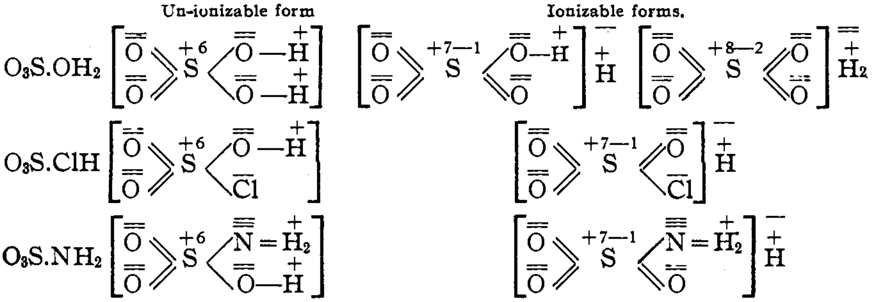
tautomeric ionizable and un-ionizable forms. This is brought out also by the organic acids which must belong to this group. With acetic acid, for instance, the tautomeric forms would be represented by



The *a* form represents the ordinary chemical non-ionizable form of acetic acid. *b* represents the ionizable form in which the carbon atom of the carboxyl group has both gained and lost an additional corpuscle and the substance exists in the tautomeric form. As far as known, carbon does not form such onium compounds readily, although as pointed out in previous papers such modes of combination must exist from indirect evidence,[1] so that the small degree of ionization of acetic acid, and, therefore, of most organic acids, may be due mainly if not entirely, to the conditions of the equilibrium, the un-ionizable form predominating greatly. With regard to the salts of organic acids, and evidently of all acids, it would appear that the conditions of the equilibria are somewhat different and that there the concentrations of the ionizable forms predominate.

In the preceding discussion, it might appear at first sight as if the difference between the tautomeric forms as postulated is the same as that assumed by Bray and Branch and by Lewis in their view of compounds with polar and nonpolar valences. From one point of view, the differences and explanations advanced are similar. From a broader point of view, considering not alone one set of phenomena but the general relations of the substances, the assumption of the existence of polar valences at one time and nonpolar valences at another, leads to contradictions, some of which were pointed out in the fifth paper.[2]

It may be of interest to formulate some of the compounds given by Werner,[3] according to the present basis:



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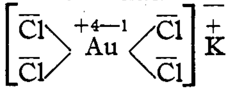
[1] IV paper, p. 1817.

[2] THIS JOURNAL, 36, 209 (1914).

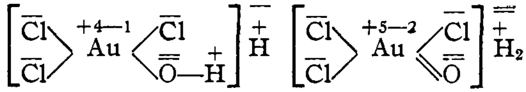
[3] *Loc. cit.*, pp. 30–1.

Un-ionizable form. Ionizable forms.

$KAuCl_4$ ....



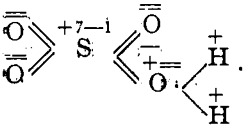
$Cl_3Au.OH_2$ ....



A detailed discussion of these substances will hardly be necessary in view of the explanations given before.

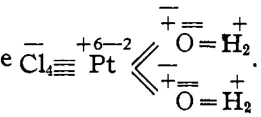
In the treatment of acids and salts given so far, the possibility of, and the relations due to tautomeric changes have been considered to a certain extent and their usefulness emphasized. It will now be necessary to consider some additional possible tautomeric changes of these compounds somewhat further, not so much because they are of importance for the substances so far considered, but because the possibility of their formation leads to relations for analogous compounds for which their existence is of importance.

In addition to the un-ionizable and ionizable structures of sulfuric acid which were given, another tautomeric form is possible involving onium compound formation of oxygen. This form may be represented by



. In this case, one of the oxygen atoms is in the onium state with a valence of $-3 + 1 = -2$. This form might be considered to be the first product formed when SO_3 and H_2O combine, the simple addition compound being represented by $O_3S.OH_2$. This then would rearrange to the tautomeric un-ionizable form, which in its turn is in equilibrium with the ionizable form. The amounts of the three forms present would then depend upon the relative stabilities of the three compounds. Whether it is possible at present to differentiate between the first addition product and its un-ionizable tautomer is doubtful and of little importance. The formulation with the onium oxygen is of importance in another connection as will appear presently.

In the formulation of the chloroplatinic acids, it was mentioned that a further possibility existed. For instance, the compound $PtCl_4.2H_2O$, ordinarily a dibasic acid, might exist in a tautomeric un-ionizable form. This form would contain an onium oxygen atom and would be analogous to the form of sulfuric acid just considered. It may also be considered to be formed by the direct addition of 2 H_2O to $PtCl_4$, each oxygen atom losing a corpuscle to the platinum and also gaining one to form the onium linking. The formula for this compound would then be



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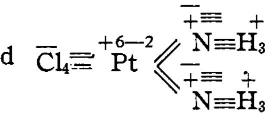
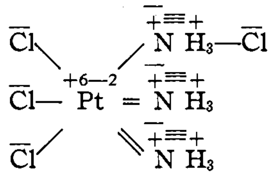
This un-ionizable form is in equilibrium with the ionizable form whose structure was given earlier. In this equilibrium, the ionizable form appears to predominate, but it is conceivable that the un-ionizable form might predominate in related compounds. All of the chloroplatinic acids might be formulated similarly, but since this would be only repetition, it will not be done here.

Platinic chloride, $PtCl_4$, combines with 2 NH_3 to form a neutral un-ionizable substance.[1] In strict analogy with the tetrachloroplatinic acid just given, this substance must be formulated

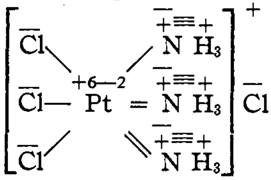


The platinum is in the same state of oxidation as before, while the nitrogen is combined with the platinum in the onium manner. The existence of tautomeric forms does not appear to be common with compounds of this type where ammonia is combined with a metallic element.

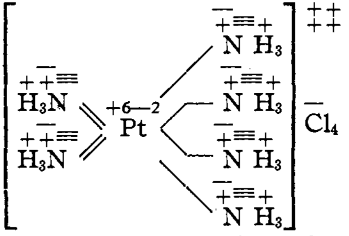
A third ammonia molecule may be introduced into tetrachlordiammine platinum. In this way, trichlortriammine platinum chloride is obtained, and ionizes into a negative chloride ion and complex positive ion. Since chlorine in direct combination with platinum is not ionized, it must follow that the ionized chlorine is in combination with nitrogen. On this basis, the following formula may be proposed for this compound:



or



The state of oxidation of the platinum is unchanged. The negatively charged chlorine combined with positively charged platinum does not ionize, but when combined with negatively charged nitrogen it does ionize. This triammine salt is capable of taking up further molecules of ammonia. For each molecule of ammonia so added, a chlorine atom becomes ionizable, until finally with six ammonia molecules present in hexammine platinum chloride, all four chlorines may be present as ions. This last compound may be formulated



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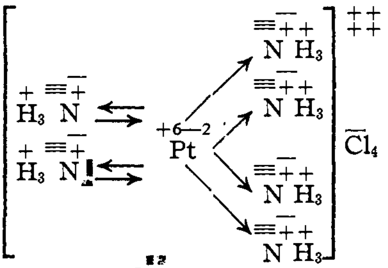
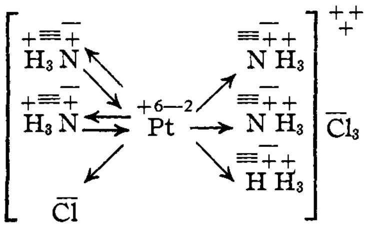
[1] Cf. Werner, *Loc. cit.*, p. 219, on the equivalence of water and ammonia as substituents.

If tautomerism were to take place with these compounds, the chlorine would be in combination with the platinum and would then not be ionizable. The reactions show that the form in which the chlorine is ionized predominates greatly in this equilibrium. The platinum atom throughout this series is neither oxidized nor reduced. The chlorine which ionizes is always in direct combination with negatively charged nitrogen.

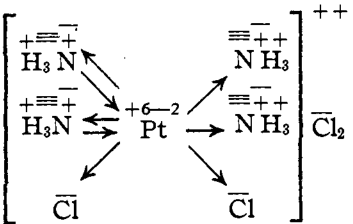
It may be of interest to formulate the complete series of platinum salts[1] in this connection. The formulas which are given represent the predominating forms present:



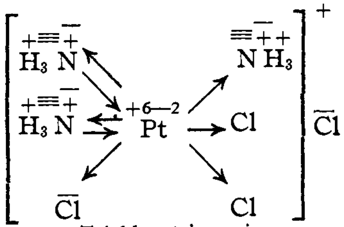
Hexammine platinum chloride.



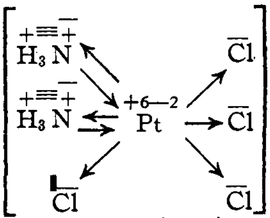
(Unknown.)



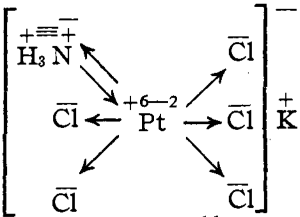
Dichlorotetrammine platinum chloride.



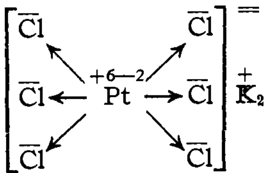
Trichlorotriammine platinum chloride.



Tetrachlorodiammine platinum.



Potassium pentachloroammine platinate.



Potassium chloroplatinate.

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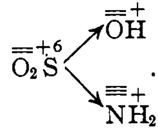
[1] Werner, *Loc. cit.*, p. 230.

In all of these compounds the valence of the platinum does not change but remains +6 — 2. The negative chloride ion is derived from the combination with negatively charged nitrogen in the onium form. Where chlorine is combined directly with positive platinum, it does not ionize. Where an ammonia molecule is combined directly with platinum with both valences forming onium linkings, no ionization appears. It is only when the nitrogen of the ammonia combines with one valence with the platinum and with the other with the chlorine to assume the onium form, that ionization of the chlorine takes place. It might perhaps be better to show in the formulas that the chloride ions in these complex platinum salts are derived from the ammonium part of the molecule and not from the platinum, but the symbolism introduced by Werner is so convenient that the formulas as given with all the charges indicated on the atoms may serve the purpose without creating confusion. The ionization of trichlorotriammine platinum chloride should follow the laws found experimentally for uni-univalent salts; of dichlorotetrammine platinum chloride, the laws for bi-univalent salts; and hexammine platinum chloride, the laws for tetra-univalent salts. The last two salts formulated above have a positively charged potassium atom in direct combination with positive platinum, and this potassium is ionized. These compounds have been discussed in sufficient detail before.

A summary of some of the relations just discussed may be of value here. The addition of ammonia to another molecule is due to its onium compound formation possibility. With $\overset{+}{H}\overset{-}{Cl}$, $\overset{+}{H}_4\overset{\overset{-}{\equiv +}}{N}\overset{-}{Cl}$ is formed. With $\overset{+6}{S}\overset{=}{O}_3$, doubtless $\overset{=}{O}_3\overset{+7-1}{S}\rightleftarrows\overset{\overset{-}{+}\equiv}{N}\overset{+}{H}_3$ is first formed and then tautomerizes to the better known



. With $\overset{+4}{Pt}\overset{-}{Cl}_4$, $\overset{-}{Cl}_4\equiv\overset{+6-2}{Pt}(\rightleftarrows\overset{\overset{-}{+\equiv}}{N}\overset{+}{H}_3)_2$ is formed and apparently does not tautomerize. Water plays an analogous part to ammonia,[1] and the relations may be formulated similarly. With $\overset{+}{H}\overset{-}{Cl}$, $\overset{+}{H}_3\overset{\overset{-\,-}{-+}}{O}\overset{-}{Cl}$ is formed. With $\overset{+6}{S}\overset{=}{O}_3$, $\overset{=}{O}_3\overset{+7-1}{S}\leftrightarrows\overset{\overset{-}{+=}}{O}\overset{+}{H}_2$ may be considered to be formed first and then to tautomerize to the forms given before. With $\overset{+4}{Pt}\overset{-}{Cl}_4$, $\overset{-}{Cl}_4\equiv\overset{+6-2}{Pt}(\rightleftarrows\overset{\overset{-\,-}{+-}}{O}\overset{+}{H}_2)$ is formed first and then rearranges to the tautomeric ionizable form. These formulas appear natural for the compounds with ammonia, but somewhat strange at first for the compounds with water. Logically they must be grouped together, although in some cases

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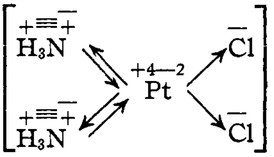
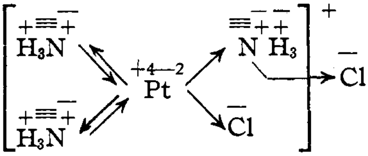
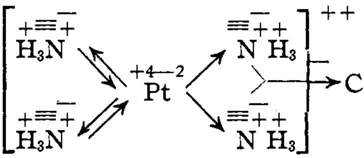
[1] Werner, *Loc. cit.*, pp. 257–64.

one set of phenomena predominates for one group in certain reactions and another set for another group in different reactions.[1]

A brief comparison of the ammonia derivatives of platinous chloride, $\overset{++-}{PtCl_2}$, with those of platinic chloride may be of interest. The series of platinous chloride ammonia compounds is as follows:[2]







In each of these compounds the platinum is in the same state of oxidation as in platinous chloride, +2. This differs in the state of oxidation from that of the platinum of $PtCl_4$, and it is only possible to pass from one series to the other by oxidizing or reducing the platinum.

The principles and relations developed for the complex platinum ammonia compounds may evidently be extended to any other compounds containing similar atoms or groups. Werner has given innumerable examples of these.

The relations of the complex ammonia salts are readily understood because the salt forming property of ammonia is so well known. If water were substituted for ammonia, similar classes and groups of compounds will be formed. The so-called basic properties of oxygen, or its ability to form onium compounds, are understood much better now than was the case relatively few years ago. If water were substituted for ammonia in $PtCl_4.2NH_3$, the resulting compound $PtCl_4.2H_2O$ tautomerizes and reacts as a dibasic acid as already explained. If water is substituted for ammonia in the platinum ammonia compounds containing more ammonia, then the water might act in the onium form just as the ammonia does. The negatively charged chlorine would then be combined with the oxygen of a water molecule, which is also combined with the platinum, and this negatively charged chlorine combined with negative oxygen would ionize. Whether such combination actually takes place with these compounds is questionable. It does, however, for such substances as hydrated

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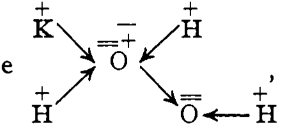
[1] It may be mentioned in this connection that the ordinary valence of the electronic point of view in which one corpuscle is transferred from one atom to another is analogous to the principal valence of Werner. The auxiliary valence of Werner corresponds in a number of compounds to the onium valence of the electronic treatment.

[2] Werner, *Loc. cit.*, p. 195.

nickel chloride, etc. The composition of the substance and the type of atoms in combination control the direction which is taken in these changes. These groups of substances include all those containing water of crystallization (or water of hydration in solution). If the water is held in onium combination, then the negatively charged element or group is combined directly with the negatively charged onium oxygen and is ionizable, while the positive ion will contain the atoms of the water molecule. Water or some similar substance must necessarily be present to bring about such ionization. This shows the importance of the solvent in ionization phenomena.

A brief discussion of the question of ionization may not be out of place here. From the considerations outlined in this paper, given in detail for a few typical substances but applicable in general, the following rule may be enunciated: *A positively charged atom ionizes only when in direct combination with an atom which contains a predominatingly positive charge; a negatively charged atom ionizes only when in direct combination with an atom which contains a predominatingly negative charge.* In $\overset{-}{Cl_6}\,\overset{+6-2}{Pt}\,\overset{+}{H_2}$, negatively charged chlorine in direct combination with positive platinum does not ionize, but positively charged hydrogen in combination with platinum carrying +6 — 2 = +4 charges, ionizes. HCl in a solvent such as benzene does not ionize. In water, from the considerations advanced before (similar to those with ammonia), the compound $\overset{+}{H_3}\,\overset{=\overset{-}{+}}{O}\,\overset{-}{Cl}$ is present.[1] The positively charged hydrogen combined with negative oxygen does not ionize, but negatively charged chlorine combined with oxygen carrying a predominatingly negative charge, ionizes. The ions here are $(H_3O)^+$ and Cl^-.[2] With potassium hydroxide in water, the compound formed would be  and the ions $(KH_2O)^+$

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[1] A greater number of water molecules may be combined with the HCl. but the principle involved would be the same.

[2] The ionization of chloroplatinic acid and of hydrochloric acid indicates that hydrogen ions in aqueous solutions may be produced in two ways. With the former, the hydrogen ionizes directly, and after being separated, combines with and is in equilibrium with water and hydronium ions. With the latter, water combines first with the hydrogen chloride and then the hydronium ion is produced by ionization. In both cases, the final equilibrium between hydronium ion, hydrogen ion, and water, is the same; but the mechanism by which this equilibrium is attained is different in the two cases. The mechanism of the ionization of ammonium salts has not been taken up in this paper. However, it may be stated, that, since ammonia and water differ only in degree in onium compound formation properties, the explanation of the ionization of ammonium salts may be based upon reasoning similar to that given for the ionization of acids.

and $(OH)^-$. The positively charged hydrogen and potassium combined with the negative oxygens are not ionized, while the negatively charged hydroxyl combined with the predominatingly negatively charged oxygen ionizes. These relations may be shown to hold generally. To go a step farther, and following Werner,[1] it may be stated that compounds of the first order do not ionize, but must go over into compounds of higher orders before ionization may appear.

An attempt is made in this paper to show the method by which the theoretical views of chemical structure based upon the classifications developed with the electron conception of valence may be used in connection with the classification based upon the relations founded on Werner's theory. It is manifestly impossible to enter into a systematic development in detail in a paper such as this. Instead, a few fundamental relations have been chosen and explained by means of typical compounds. A study of Werner's "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie" on the basis of these relationships will show a large number of applications and extensions of these views to related compounds. It is believed that the views developed here and explained in connection with Werner's classifications add certain ideas to the latter, and especially bring out, perhaps in ways not evident before, a connection between the valence structures of inorganic and organic compounds. As a first exposition of these views it is to be expected that uncertainties and questionable points with regard to individual compounds and perhaps to some of the generalizations will appear, but on the whole, the further development of the views outlined appears to promise useful classifications of the compounds of inorganic chemistry as a branch of chemistry in general.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A SEARCH FOR AN ALKALI ELEMENT OF HIGHER ATOMIC WEIGHT THAN CESIUM.

BY GREGORY PAUL BAXTER.

Received December 10, 1914.

Two years ago the writer was fortunate enough to secure a considerable quantity of pollucite, which was obtained in the Paris, Maine, region. The material contained, approximately, 33% of cesium, rubidium and potassium oxides, chiefly cesium oxide, besides about 2% of lithium and sodium oxides. Through the assistance of Mr. C. C. Wallace the bases were extracted from the mineral by fine grinding and digesting with concentrated nitric acid. Treatment of the silicic acid residue with hydrofluoric acid showed that the extraction with nitric acid was very nearly complete.

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[1] *Loc. cit.*, p. 89.