

would not be as satisfactory an absorbent for ammonia for practical use as those described by Foote and Hunter,<sup>2</sup> Foote and Brinkley<sup>2</sup> and Davis, Olmstead and Lundstrum.<sup>2</sup>

### Summary

1. The vapor-pressure curve at 0° for the system ammonia:mercuric cyanide has been determined from 369 to 1615 mm.

2. The solubility curve of the ternary system ammonia:mercuric cyanide:water has been determined at 0°.

3. The vapor pressures of the solutions are far below those required by Raoult's law.

4. The solid addition products,  $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3$  and  $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$ , have been isolated and have been shown to be the only ones formed at 0°.

NEW HAVEN, CONNECTICUT

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## THE CONSTITUTION OF METALLIC SUBSTANCES

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### I. Introduction

Recent advances in our knowledge of the structure of the atoms and of crystalline substances have made it possible to render a fairly satisfactory account of the constitution of salts and of many non-metallic compounds. The constitution of metallic elements and metallic compounds, however, remains almost as obscure as heretofore. Indeed, few writers have ventured to hazard a guess as to the nature of these interesting substances.

Approximately 80% of the known elements are metallic in the free state, and all compounds between distinctly metallic elements are metallic. In addition, many compounds between metallic and non-metallic elements are likewise metallic. The metals thus include a large number of important substances. The study of metallic substances has received little attention, particularly from the chemical point of view. It is only recently that methods have been developed as a result of which we now have information relative to the composition of metallic compounds. Even now, many simple systems have not been systematically studied, while the more complex systems have scarcely been touched upon except in a few instances. The physical and chemical properties of metallic compounds are little known even from a qualitative standpoint. Data relative to the energy changes accompanying the formation of metallic compounds are very meager. It is apparent that at the present time the metals constitute a great field which remains practically undeveloped.

Before proceeding to a discussion of the constitution of metallic sub-

stances, it will be advantageous to consider, briefly, the metallic state of matter, in general. The uniform occurrence of certain properties in different metallic substances indicates some common feature underlying their constitution. According to modern views, the metals owe their characteristic properties chiefly to the negative electrons which are free to move within the body of the metal. Much of our knowledge relative to the existence of free negative electrons in metals is derived from indirect evidence. The most direct evidence as to the existence of negative electrons in metallic elements has been obtained from a study of solutions of the alkali metals in liquid ammonia. This solvent constitutes the only non-metallic medium in which metals are soluble. Solutions in ammonia, therefore, constitute the only means we have for obtaining an insight into the influence of concentration on metallic properties. In what follows it will be necessary to draw largely on the results obtained from the study of solutions in this solvent.

The properties of a given system, as regards its chemical behavior, depend largely upon the tendency which the constituent elements possess for combining with negative electrons to form stable complexes. Electronegative elements owe their characteristic property of functioning as anions to the fact that they form stable complexes with one or more negative electrons. This union of the negative electron with an electronegative element or group of elements is a relatively stable one, and persists throughout the various compounds in which this element or group of elements occurs. It is only with great difficulty that these complexes may be broken down. Since, under these conditions, the negative electrons are firmly attached to atomic groups, they possess freedom of motion only insofar as these groups, as a whole, are capable of moving under given conditions. Metallic properties are therefore lacking in such compounds. Only such substances may be expected to exhibit metallic properties as do not contain sufficient electronegative elements to engage the negative electrons supplied by the more electropositive constituents, or, otherwise, in which uncombined electronegative elements are lacking.

Any element or group of elements which is capable of forming a stable complex with the loss of one or more negative electrons possesses, in a sense, metallic properties. Whether a given system containing such groups will be metallic depends upon whether or not other more electronegative constituents are present to combine these electrons. The smaller the affinity of an element or group of elements for the negative electron, the more electropositive will the element or group appear, and the more readily will it enter into reaction with more electronegative elements.

According to this view, the metallic elements are to be looked upon as salt-like substance in which the negative electron appears as electronegative constituent. Chemical reactions in which these elements are con-

cerned consist essentially in a combination of the negative electron with an electronegative element or group of elements. The energy effects accompanying such reactions are largely due to the reaction taking place between the negative electron and the electronegative constituent to form a negative ion. This will be the more true, the more electropositive the metallic constituent and the more electronegative the electronegative constituent. Compounds between strongly electronegative and electropositive constituents, therefore, should invariably form salts or salt-like substances. On the other hand, compounds between strongly electronegative elements and only weakly electropositive elements may be expected to yield substances in which the salt-like properties are subordinate.

It should further be borne in mind that the properties of a substance depend upon its state. This is particularly true of metallic properties. These properties are extremely sensitive to a slight change in the environment of the substance. For example, the specific resistance of a metal is very sensitive to change of temperature, pressure and other factors. The metallic state of an element is particularly dependent upon its concentration. This will be clear when it is recalled that the vapors of metallic elements are throughout non-metallic. Thus, mercury vapor under ordinary conditions is a non-conductor; and even at high temperatures and at densities comparable with those of the metal, mercury vapor is a very poor conductor.<sup>1</sup> In the case of electrolytes, it is well known that the properties are dependent upon concentration, particularly when dissolved in solvents of low dielectric constant. While the salts in the pure state exhibit a high equivalent conductance, dissolved in solvents of low dielectric constant, such salts exhibit an extremely low conducting power. So, also, salt vapors exhibit only a very low conductance. We may conclude, therefore, that the properties of salt-like substances, and the metals may be included in this class, will vary largely as a function of concentration. That this important fact should have escaped observation in the case of metals is not surprising, since, as a rule, metals are not soluble in non-metallic liquids.

It is unsafe to draw conclusions relative to the constitution of chemical compounds from their behavior in the solid state, for it is well known that in this state the various elements of the compound exist under the action of forces which tend to arrange them in a compact and orderly manner, more or less irrespective of the nature of the forces which may be operative under other conditions. It would appear that the constitution of compounds could be successfully studied only in the liquid or vapor state at relatively low concentrations, where interacting forces, except such as are primarily concerned in forming the compounds themselves, are practically eliminated. If, therefore, we wish to determine

<sup>1</sup> Strutt, *Phil. Mag.*, 4, 596 (1902).

the constitution of metallic substances, it will be necessary to obtain these substances in a non-crystalline state at low concentrations. In the case of strongly electropositive elements, it is to be expected that the properties will vary gradually from those of a metal to those of an electrolyte or salt, as the concentration of the metal decreases. At very low concentrations, assuming that no other substances are present, it is to be expected that the metallic atom will be a neutral complex possessing no metallic properties. If, on the other hand, an ionizing medium were present, we should expect certain properties of the electronic compound to persist. Since salts are ionized in electrolytic solvents at low concentrations, we should expect the metals to be ionized under similar conditions, and the ionization should vary as a function of the concentration in a similar manner. It is possible, and indeed probable, that at very low concentrations the negative electron will no longer possess that freedom of motion which is characteristic of the metallic state. For, even though the solvent molecules were incapable of forming a stable complex with the negative electron, it is to be expected that, owing to the action of their field, the electrons would be associated with the solvent molecules with a consequent reduction of their mobility. This is known to be the case in gaseous systems, where the negative electron may readily be formed by means of external radiations. At ordinary pressures, the mobility of the negative electron is as low as, or even lower than, that of positive ions. It is only at low concentrations of the gas that the mobility of the negative electron becomes comparable with that which might be expected of free electrons. It may be expected that in many instances the negative electron will form more or less stable complexes with the solvent medium, in which case, practically, salts will be formed. Such systems will not be metallic at high concentrations.

The question to be determined is this: what elements are capable of forming stable complexes with negative electrons? Let us suppose, for example, that both sodium and tin were soluble in a given solvent. What would be the properties of such a solution at low concentrations? While in the pure state, tin is a metallic element which presumably furnishes free negative electrons in this state; on the other hand, it is well known that tin forms many compounds which are relatively non-salt-like in property.<sup>2</sup> Is it not conceivable, therefore, that in such a mixture tin would associate itself with the negative electron to form a stable complex, namely, a tin anion? It is well known that sodium and tin form a series of relatively stable compounds. Assuming the existence of a solvent in which these compounds were soluble, we may inquire as to what would be the properties of these solutions. From what has already been said, it is clear that, whatever the nature of these compounds may be,

<sup>2</sup> For example, stannic chloride.

it is not to be expected that dilute solutions of such compounds will be metallic. Even solutions of the alkali metals themselves, in the presence of a non-reactive solvent, in other words, a solvent with which the alkali metals form no compounds, lose, to a large extent, their characteristic metallic properties at low concentrations. We are led to conclude that solutions of metallic compounds at low concentrations will exhibit purely non-metallic properties, or, possibly, salt-like properties, since it is conceivable, or even probable, that the more electronegative metallic elements may form stable complexes with negative electrons supplied by the more electropositive metals. We may inquire whether there are available any facts indicating that compounds of strongly electropositive elements with less electropositive metallic elements are salt-like in character. As will be shown below, numerous metallic compounds exist whose properties are fully in harmony with this view.

## II. The Negative Valences of Metallic Elements

According to present views regarding the structure of matter, elementary substances (excepting elements of the argon group) may be expected to exhibit either electropositive or electronegative valence. The conception has frequently been employed in accounting for the structure of compounds among non-metallic elements but appears not to have been extended to compounds among metallic elements. *A priori*, there is no reason why an element which ordinarily exhibits a fairly strong electropositive valence might not be expected to exhibit, likewise, a fairly strong electronegative valence. This is unquestionably the case with hydrogen which, in combination with strongly electronegative elements, appears to be positively charged or, at any rate, is associated with the positive ion, while in the hydrides of the strongly electropositive elements it is negatively charged.<sup>3</sup>

The normal compounds of the strongly electropositive elements with sulfur, selenium and tellurium are non-metallic. On the other hand, similar compounds with arsenic, antimony and bismuth are metallic. The greater the atomic number of an element, and the farther it lies removed from the seventh group of elements, the more pronounced are the metallic properties of its compounds with more electropositive elements. So, the compounds of the alkali metals with antimony and bismuth are more metallic than those with arsenic and phosphorus. Similarly, the compounds of sodium with mercury and lead are more distinctly metallic than those with bismuth and tellurium. Sodium forms with antimony the compound  $\text{Na}_3\text{Sb}$ . There is no reason for believing that this compound differs essentially from the nitride  $\text{Na}_3\text{N}$ , or the phosphide  $\text{Na}_3\text{P}$ , on the one hand, or from the sulfide  $\text{Na}_2\text{S}$  or the telluride  $\text{Na}_2\text{Te}$ , on the other.

<sup>3</sup> Moers, *Z. anorg. Chem.*, **113**, 179 (1920).

In the fourth group, lead and tin form stable compounds,  $\text{Na}_4\text{Pb}$  and  $\text{Na}_4\text{Sn}$ , in which these elements may be assumed to exhibit a negative valence of 4. It appears, then, that the elements of the sixth group exhibit a marked negative valence of 2, those of the fifth group of 3, and those of the fourth group of 4. The compounds in which the elements appear combined according to these proportions are relatively very stable, as is indicated by their melting-point diagrams, and the heat effects accompanying their formation. While the compounds of the heavier metals of the fourth and fifth groups are metallic, those of the sixth groups are non-metallic. It follows that the compounds of the elements of the various groups are essentially of the same nature. In other words, the property of metallicity does not involve a fundamental difference between the structure of such compounds and the structures of non-metallic compounds.

The question may be raised: if the more electronegative elements in metallic compounds are, in fact, negatively charged, why have we no data which indicate the existence of such negative ions? The answer to this question is obvious; the compounds in question have not been studied under conditions in which such properties might be expected to be disclosed. As we shall see below, under suitable conditions, compounds of this type yield conclusive evidence of the existence of negative ions of metallic elements.

### III. Complex Negative Ions of Metallic Elements

A difficulty which confronts any theory of the constitution of metallic compounds lies in the multiplicity of compounds derivable from a single pair of metallic elements. Thus sodium and tin form the compounds  $\text{Na}_4\text{Sn}$ ,  $\text{Na}_2\text{Sn}$ ,  $\text{Na}_4\text{Sn}_3$ ,  $\text{NaSn}$  and  $\text{NaSn}_2$ . Writers on this subject have been misled in that they have looked upon the compositional formulas as indicative of the constitution of these compounds. When such writers have expressed an opinion as to the nature of such compounds they have, as a rule, been inclined to take the position that in these compounds the atoms are held together by forces essentially different from those operative in the case of non-metallic compounds.<sup>4</sup> Too much emphasis has been placed upon the proportions in which the various atoms combine. Apparently, no attempt has been made to discover to what extent the various atoms entering into metallic compounds exist in the same condition. In a compound of the type  $\text{NaSn}_2$ , for example, are all the tin atoms present in the same condition, in other words, are all the tin atoms of this compound equivalent; or do these compounds possess a definite structure in which the relation of tin atoms to the sodium atoms differs for different atoms?

The argument will perhaps be clearer when it is recalled that the tendency

<sup>4</sup> Tammann, "Lehrbuch der Metallographie," Leopold Voss, 1914, p. 230.

of relatively electronegative atoms to form stable negatively charged complexes is very pronounced. Thus, we have such complexes as the sulfate ion, nitrate ion, chlorate ion, perchlorate ion, etc. In these complexes the elements are arranged in a definite manner under all conditions, whether in the solid or the fused state or in solution. Furthermore, the nature of these complexes is not materially affected by the nature of the electropositive constituent with which they appear combined. Very striking, for example, is the trinitride ion,  $N_3^-$ , in which three nitrogen atoms appear combined to form a stable, singly charged complex anion. This tendency of electronegative elements to form complexes is one much more common than has hitherto been suspected. This is particularly true of complexes in which a single element is concerned. The most familiar example of this type of complex anion is the tri-iodide ion. It has been shown that it is a general property of the iodide ion to associate with itself two additional atoms of iodine to form a relatively stable complex. In solution, an equilibrium exists between the simple iodide ion and the complex ion. In the solid state the iodides include  $MI$ ,  $MI_3$ ,  $MI_5$ ,  $MI_7$  and  $MI_9$ , where  $M$  is a univalent element.<sup>5</sup> Among other elements which exhibit a similar tendency to form complex ions, only the complex sulfide ion has been studied extensively.<sup>6</sup> It has been shown that the normal sulfide ion takes up additional sulfur to form a series of complex anions,  $S_2S^{--}$ ,  $S_3S^{--}$ ,  $S_4S^{--}$ ,  $S_5S^{--}$ . Thus far, the complex sulfides have been studied only in aqueous solution. However, this property of the sulfide ion to form complexes with additional sulfur atoms is not restricted to aqueous solutions, but is one common to sulfides in numerous solvents. There is evidence indicating that selenium and tellurium similarly form complex ions, although only the complex telluride ion has been studied in some detail in aqueous solution.<sup>7</sup> May we not infer that other elements than those of the sixth and seventh groups exhibit a pronounced tendency to form complex anions? This hypothesis would account, for the most part, for the large number of compounds formed from a single pair of metallic elements.

We may, indeed, proceed one step further and suggest that the atoms in an elementary substance do not all function in the same manner. Is it not conceivable that many elements are, in effect, compounds in which certain atoms act electropositively and others electronegatively? This would account for many of the properties of the less distinctly electropositive metallic elements.

<sup>5</sup> Abel and Halle, Abegg's "Handbuch der anorganischen Chemie," S. Hirzel, 1913, IV, 2, p. 432.

<sup>6</sup> Küster and Heberlein, *Z. anorg. Chem.*, **43**, 53 (1905); Küster, *ibid.*, **44**, 431 (1905); **46**, 113 (1905).

<sup>7</sup> Tibbals, *THIS JOURNAL*, **31**, 902 (1909).

#### IV. The Nature of Metallic Substances Dissolved in Liquid Ammonia

One of the great difficulties encountered in the study of the nature of metallic substances lies in the fact that these substances can be obtained only in the pure state or dissolved in other metallic substances. It is difficult, therefore, to determine to what extent the properties of the resulting system are due to a given constituent. As has already been pointed out, the state of a system is largely dependent upon its concentration. If the concentration of a given constituent may be altered by the introduction of a second constituent whose properties differ markedly from those of the first, then a study of the manner in which the properties of the first constituent vary as a function of concentration yields important information as to the nature of the substance in question. Thus far, only a single class of solvents has been discovered in which metallic substances are more or less generally soluble, namely, liquid ammonia and the amines. In addition to the alkali metals and the metals of the alkaline earths, liquid ammonia dissolves a number of metallic compounds.<sup>8</sup>

Let us consider, first, the properties of metallic elements dissolved in liquid ammonia. It has been conclusively shown that solutions of the strongly electropositive elements in liquid ammonia exhibit properties intermediate between those of metals and electrolytes, the properties varying continuously as a function of concentration.<sup>9</sup> At very low concentrations, a solution of an element is virtually a solution of a salt, for in these solutions the positive ion exhibits all the properties characteristic of an ion of a normal salt, while the negative ion exhibits many properties similar to those of anions of typical electrolytes. The conducting power of the negative ion, for example, is comparable with that of ordinary negative ions. In other respects, the properties of the negative ion in dilute solutions of the metals in ammonia differ materially from those of typical electronegative ions in the same solvent. The chief difference lies in the fact that, in the typical anions, the negative electron is firmly associated with an electronegative element or group of elements, whereas in an ammonia solution of a metal the negative ion consists essentially of a negative electron rather loosely associated with ammonia molecules. The electrolytic character of different metallic elements is clearly exhibited in the ionization equilibria in ammonia solution. The conductance curves of solutions of the metals in ammonia at low concentrations are practically identical in form with those of typical salts of the same metals in this solvent. Assuming the degree of ionization to be measured by the ratio of the equivalent conductance at a given concentration to the limiting value which the equivalent conductance approaches at low concentration, the ionization of typical metals in liquid ammonia is practically the same as that of the correspond-

<sup>8</sup> Kraus, *THIS JOURNAL*, 29, 1557 (1907).

<sup>9</sup> Kraus, *ibid.*, 43, 749 (1921); 36, 864 (1914); 30, 1323 (1908).



ing salts in the same solvent. Unquestionably, in solutions of metals in liquid ammonia we are dealing with equilibria similar to those in solutions of the corresponding salts.

Indeed, we not only have equilibria between different metals in ammonia solution; we also have equilibria between the metals and typical salts in this solvent. Solutions of metals in the presence of salts of other metals do not yield reaction products when these products are soluble. When an insoluble product may be formed, however, this product is precipitated. Thus, metallic calcium reacts with potassium chloride metathetically according to the reaction equation  $2KCl + Ca = CaCl_2 + 2K$ , insoluble calcium chloride being precipitated and metallic potassium remaining in solution. If a salt of a metal insoluble in ammonia is added to a solution of a metal, the insoluble metal is precipitated. Thus  $AgI + Na = NaI + Ag$ , silver being precipitated. In many instances, however, the precipitated metal itself is capable of forming anions, in which case a compound of the two metals is precipitated. Thus  $BiCl_3 + 6Na = 3NaCl + Na_3Bi$ , the bismuthide being precipitated as a metallic compound. The behavior of solutions of the metals in ammonia is similar to that of solutions of salts. We may conclude, therefore, that at low concentrations the metals are, in fact, salt-like in character.

At higher concentrations, certain properties of the metal solutions begin to diverge markedly from those of solutions of non-metallic substances. This change in the properties of solutions of metallic substances is to be ascribed, primarily, to the fact that the negative electron is freed from its association with atoms or groups of atoms at high concentrations. As a consequence, the conductance of solutions at higher concentrations becomes sufficiently great to impart to them distinctly metallic properties. There is nothing to indicate that the nature of the metal in solution has been greatly altered at higher concentrations. In other words, at higher concentrations, the electropositive constituent continues to exist as a positive ion, while the electronegative constituent yields free negative electrons as a result of which the metallic properties appear. What portion of the total number of negative electrons in a metallic element at higher concentrations actually takes part in the conduction process cannot be stated. It is not unlikely that, in the alkali metals, the greater portion of the negative electrons are in a condition in which they are capable of carrying the current.

If the metallic elements themselves are salt-like in character, then there is all the more reason for believing that metallic compounds likewise are salt-like, particularly, compounds in which one of the elements is strongly electropositive and the other strongly electronegative. Here, again, solutions in liquid ammonia supply definite information relative to the constitution of metallic substances. Various compounds of the alkali

metals with the heavy metals of the fourth, fifth and sixth groups are very soluble in liquid ammonia. In general, the solutions of such metallic compounds are characteristically colored, but they exhibit no marked metallic properties except, possibly, at very high concentrations.<sup>8</sup> So, for example, concentrated solutions of a compound of sodium and lead exhibit a distinct metallic luster, somewhat of a violet tint.

The important question to be answered is: what is the nature of these metallic compounds in solution? In the first place, it is to be noted that the process of solution and precipitation of such metallic compounds is a reversible one and is accompanied by a relatively small energy change, which indicates that, if ammonia is associated with these compounds in solution, such association is purely of a secondary nature. There is nothing to indicate that the compounds in solution differ materially in nature from the same compounds in the solid state. If metallic compounds are salt-like in character, we should expect that in solution, at low concentrations, the more electropositive element would be present as a normal cation and the electronegative element as an anion. By analogy, we should expect the metals of the sixth group to form divalent anions, of the fifth group trivalent anions, and of the fourth group quadrivalent anions. Whether the metals of the third group form quinquivalent anions is uncertain, since only thallium forms a soluble compound, and its solubility is so low that its nature cannot readily be determined.<sup>10</sup> It is possible, too, that the negative valence of a metallic anion may be variable, just as the positive valence of the same metal is often found to be variable. This tendency to variation in electronegative valence, if it exists, might be expected to become more pronounced as the element becomes more electropositive.

Whether a solution of a compound is an electrolyte is readily determined by subjecting it to electrolysis. Sodium reacts with metallic lead in liquid ammonia, giving a solution containing approximately 2.25 atoms of lead per atom of sodium.<sup>11</sup> Leaving aside for the moment the precise nature of the compound in question, we should expect that, if the lead is associated with the anion, 2.25 atoms of lead would be precipitated on the anode when one equivalent of electricity passes through the solution. That solutions of the sodium-lead compounds are electrolytes was shown by Kraus<sup>9</sup> and later by Posnjak and by Smyth.<sup>11</sup> In these solutions approximately 2.25 atoms of lead are precipitated on the anode, corresponding to the mean composition of the solution. Without question, lead is present in these solutions as a negative ion. That antimony is present as an anion in liquid ammonia was shown by Peck,<sup>12</sup> although

<sup>10</sup> Unpublished observations by Mr. H. F. Kurtz in this Laboratory.

<sup>11</sup> Smyth, *THIS JOURNAL*, 39, 1299 (1917).

<sup>12</sup> Peck, *ibid.*, 40, 335 (1918).

owing to the difficulty of precipitating the antimony on the anode in coherent form, the results of electrolysis do not agree with the composition of the solution as satisfactorily as in the case of lead.

The nature of the complexes formed between sodium and tellurium in liquid ammonia solution has been studied in some detail in this Laboratory.<sup>13</sup> Briefly, when metallic tellurium is introduced into a solution of sodium in liquid ammonia, reaction takes place with great facility, resulting in the formation of the normal telluride,  $\text{Na}_2\text{Te}$ , which is largely precipitated as a white, slightly crystalline non-metallic substance. This telluride is slightly soluble, and, in the presence of metallic tellurium, reacts further to form complex tellurides. In the first stage of the reaction the compound  $\text{Na}_2\text{Te}_2$  is formed, the composition of the solution in equilibrium with the normal telluride corresponding to this formula. In the presence of excess tellurium, the normal telluride goes completely into solution, forming a complex which probably has the composition  $\text{Na}_2\text{Te}_4$ , since this corresponds very closely with the mean composition of the solution at higher concentrations.

The properties of the complexes formed depend upon the amount of tellurium associated with the anion. The normal telluride, as already mentioned, is a non-metallic substance, only slightly soluble in liquid ammonia. The compound  $\text{Na}_2\text{Te}_2$  is extremely soluble in liquid ammonia and forms a deep violet-blue solution. When precipitated from solution, this complex exhibits metallic properties. The compound  $\text{Na}_2\text{Te}_4$  is likewise extremely soluble, forming a deep red solution in liquid ammonia, and this compound, also, is metallic when precipitated. It is interesting to note that the introduction of additional tellurium into the anion complex converts the normal non-metallic telluride to a metallic substance. At very low concentrations, the proportion of tellurium present in a solution in equilibrium with metallic tellurium falls below the value corresponding to the formula,  $\text{Na}_2\text{Te}_4$ , but at high concentration the composition of the solution approaches a value corresponding to that of this compound very closely. It may be inferred that at low concentrations an equilibrium exists between two or more complexes; as, for example,  $\text{Na}_2\text{Te}_4$  and  $\text{Na}_2\text{Te}_2$ . This is not unexpected, since the ionization and possibly other fundamental properties of the compound undergo alteration as the concentration decreases. In this, the behavior of the compound does not differ materially from that of the corresponding complex sulfides and iodides in aqueous solution.

It remains to determine definitely the constitution of the complex telluride anion. This can be done by molecular-weight determinations only. While the determination of molecular weights at higher concentrations is very uncertain, owing to the fact that the laws of dilute solutions are

<sup>13</sup> C. Y. Chiu, *Dissertation*, Clark University, 1920.

not applicable and the laws governing the equilibria in such systems are unknown; by determining the apparent molecular weight at a series of concentrations and thus determining the manner in which this quantity varies as a function of the concentration, an inference may be drawn as to the probable complexity of the substance in solution. Such a study has been carried out in this Laboratory, as a result of which it appears that the anion carries two negative charges.<sup>14</sup> Presumably, the anion consists of a normal telluride ion  $\text{Te}^{--}$  associated with additional tellurium. There are thus in solution under various conditions the anions:  $\text{Te}^{--}$ ,  $\text{TeTe}^{--}$ , and  $\text{Te}_3\text{Te}^{--}$ . This view of the constitution of the complex telluride ion is in harmony with the accepted theory of the constitution of the complex sulfide ion.<sup>15</sup>

Peck<sup>12</sup> has shown that antimony forms a series of complex anions in liquid ammonia solution in the presence of a sodium ion. The initial compound here precipitated has the composition  $\text{Na}_3\text{Sb}$ , corresponding with the normal electronegative valence of antimony. It is interesting to note that, while the normal telluride is non-metallic, the normal antimonide is metallic. The normal antimonide is only slightly soluble in liquid ammonia. In the presence of excess antimony, the mean composition of the solution varies as a function of concentration. At a concentration 0.0049 *N* in sodium, the atomic ratio of antimony to sodium in solution is 1.198, differing thus very little from a proportion of one atom of antimony to one atom of sodium. At higher concentrations the proportion of antimony to that of sodium increases, reaching a maximum of 2.333 atoms of antimony per atom of sodium at a concentration 0.4347 *N*. At still higher concentrations, the proportion of antimony to sodium decreases slightly.

The complexity of the anion in the antimony solutions has not been determined, but it appears probable that the nature of the anion in antimony solutions does not differ materially from that of the corresponding ion in tellurium solutions. Accordingly, the antimony anion carries 3 negative charges, corresponding to those of the normal antimonide ion. Otherwise, it would be necessary to assume that the electronegative valence of antimony changes as a function of the proportion of antimony present in the solution. This assumption appears improbable. The highest atomic ratio in the antimony solutions corresponds to the formula  $\text{Na}_3\text{Sb} \cdot \text{Sb}_6$ .

The ratio of sodium to lead in the lead solutions, as already stated, is approximately 2.25 atoms of lead per atom of sodium, and this ratio appears to be independent of the concentration. The normal plumbide is  $\text{Na}_4\text{Pb}$ . Unless the electronegative valence of lead changes, as additional

<sup>14</sup> E. H. Zeitfuchs, *Dissertation*, Clark University, 1921.

<sup>15</sup> Küster and Heberlein, Ref. 6.

lead is combined with the anion, the complex in solution corresponds to the formula  $\text{Na}_4\text{Pb}_3\text{Pb}_8$ .

In the accompanying figure the ratio of antimony to sodium is represented by Curve A, that of tellurium to sodium by Curve B, and that of sulfur to sodium in aqueous solutions by Curve C. The similarity of the curves is unmistakable.

The results above given clearly show that solutions of compounds of the less electropositive metallic elements with strongly electropositive

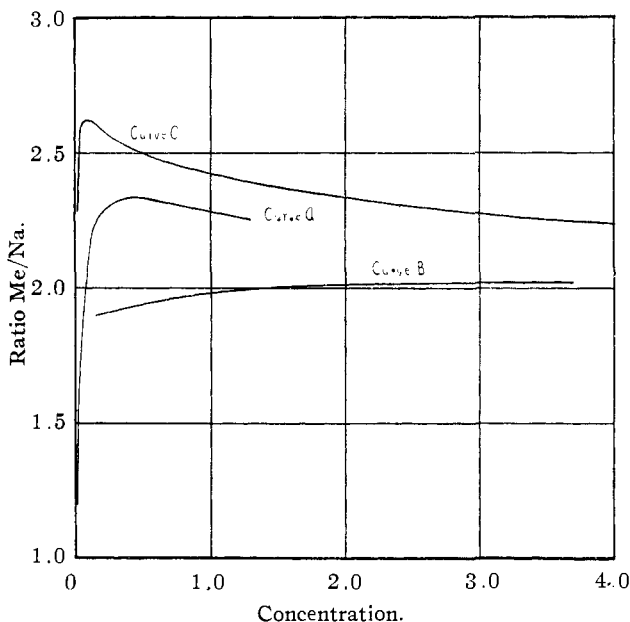


Fig. 1.—The change in the compositions of solutions due to complex formation.

metallic elements are electrolytes, the more electronegative element forming an anion, the number of charges on which corresponds with its position in the periodic system. In the presence of excess of the less electropositive metal, the normal anion reacts with the free metal to form complex anions. The property of tellurium, selenium, antimony, bismuth, lead and tin to form complex anions indicates that this property is in all likelihood a general property of metallic, as well as of non-metallic elements. Indeed, if anything, this property is more pronounced in the more metallic elements than it is in the less metallic elements. That the solutions of the compounds in question are electrolytic may be accepted as an established fact. If the solutions of these substances are electrolytic, then it seems possible, and indeed probable, that the compounds themselves in a free state are salt-like in character; that is, the more

electropositive element is present as cation and the more electronegative element as a more or less complex anion. In what manner the metallic properties of these substances are related to their constitution still remains uncertain. In the case of the tellurium compounds, however, the conclusion seems inescapable that the metallic properties are due to the excess of tellurium atoms in the complex anion, for the normal telluride itself is non-metallic while the complex tellurides are metallic. It should be borne in mind that, while the negative electrons are firmly attached to the electronegative constituent at low concentrations, some of these electrons may readily become movable at high concentrations, for the pure element itself is metallic. At sufficiently high concentrations of the metal or in the pure state, various interactions arise between the charges present in the molecular complex, as a result of which the negative electrons, in part at least, acquire freedom of motion.

#### V. Reaction of Metallic Compounds in Liquid Ammonia Solution

The behavior of solutions of metallic compounds in liquid ammonia clearly indicates that these substances are true electrolytes. They exist in solution in equilibrium with other electrolytes as do ordinary salts and they react with other electrolytes in a similar manner. They undergo metathetical reactions the course of which is determined by the solubility of the compounds formed. With ordinary salts they form metallic compounds which are precipitated from solution when these are insoluble, while they remain in solution when soluble. Thus the lead compound reacts with a cadmium salt according to the equation,  $\text{Na}_2\text{Pb} + \text{Cd}(\text{NO}_3)_2 = 2\text{NaNO}_3 + \text{CdPb}_x$ , the compound  $\text{CdPb}_x$  being precipitated. Whether this compound will remain as such after precipitation depends upon its stability and on other factors. This point has not, as yet, been fully cleared up. On the other hand, with metallic calcium, a reaction takes place according to the reaction equation,  $\text{K}_2\text{Pb}_x + \text{Ca} = \text{CaPb}_x + 2\text{K}$ . Here calcium plumbide is precipitated while metallic potassium remains in solution.<sup>11</sup> With an ammonium salt the following reaction occurs:  $\text{NaPb}_x + \text{NH}_4\text{I} = \text{NaI} + \text{NH}_4\text{Pb}_x$ . The resulting plumbide, however, is unstable, as might be expected, and decomposition occurs at once on precipitation with the formation of ammonia and the evolution of hydrogen, while pure lead is left behind.

Very interesting is the case in which an electronegative ion of a metal is precipitated by means of an electropositive ion of the same metal. For example, sodium plumbide, on the addition of lead nitrate, precipitates lead according to the equation,  $\text{Na}_4\text{Pb}_9 + 2\text{Pb}(\text{NO}_3)_2 = \text{Pb}_2\text{Pb}_9 + 4\text{NaNO}_3$ . The precipitated lead may here be looked upon as a lead plumbide. Whether or not the various lead atoms in the resulting precipitate are equivalent to one another or whether they differ remains

undetermined. It is conceivable that, in the case of metals which are fairly electropositive and which, at the same time, exhibit a pronounced electronegative valence, the metal in the pure state may exist in the form of a compound, a portion of the atoms being positively charged and another negatively charged. Many facts are in harmony with such an hypothesis. It is well known that the more electronegative elements, such as selenium,<sup>16</sup> tellurium,<sup>17</sup> arsenic<sup>18</sup> and antimony,<sup>17,18</sup> are complex in the vapor state. It is not unreasonable to assume that in these complexes some of the atoms function electropositively and others electronegatively. Furthermore, if these elements are complex in the vapor state, then there is all the more reason for believing that they are likewise complex in the liquid state and, indeed, in this state their complexity may be expected to be relatively high. It is well known that sulfur in the liquid state is complex and certain facts indicate that selenium and tellurium in the solid state are complex. Naturally, the complexity of vapors varies as a function of the temperature, the more complex molecules breaking down at higher temperatures. It appears probable that in these complexes the various atoms are not identically involved.

This hypothesis is in harmony with many facts relating to liquid and solid metals. If the values of the equivalent conductance of various metallic elements are compared at ordinary temperatures, it will be found that the strongly electropositive elements are the best conductors, while the more electronegative metallic elements are relatively very poor conductors. The question arises: to what is the difference in the conductance of the various elements to be ascribed? Is it due entirely to a difference in the resistance which the electrons experience in their motion, or is it in part due to the fact that a smaller number of electrons are available in a given volume? If compounds are formed between different atoms of a given element, some of which are charged positively and others negatively, then we should expect that those elements which exhibit the greatest tendency to form compounds of this type would exhibit the lowest equivalent conductance. In the following table are given values of the equivalent conductances of various metallic elements.

TABLE I  
EQUIVALENT CONDUCTANCES OF SOME METALLIC ELEMENTS

Metal	Eq. Cond. $\times 10^6$	Metal	Eq. Cond. $\times 10^5$
Silver.....	6.999	Zinc.....	0.856
Potassium.....	6.503	Indium.....	0.635
Sodium.....	5.288	Strontium.....	0.360
Rubidium.....	4.845	Thallium.....	0.326
Copper.....	4.559	Tin.....	0.313

<sup>16</sup> Brockmüller, *Z. physik. Chem.*, **81**, 129 (1912).

<sup>17</sup> Dobbie and Fox, *Proc. Roy. Soc.*, **98A**, 149 (1921).

<sup>18</sup> Biltz and V. Meyer, *Z. physik. Chem.*, **4**, 263 (1889).

Gold.....	4.547	Lead.....	0.2305
Cesium.....	3.898	Antimony.....	0.1553
Magnesium.....	1.607	Arsenic.....	0.1245
Lithium.....	1.534	Mercury.....	0.0782 (liquid)
Aluminum.....	1.278	Gallium.....	0.0736
Calcium.....	1.228	Bismuth.....	0.0657
Cadmium.....	0.937		

It will be observed that the metals of the first group and the metals of the alkaline earths possess the highest conducting power. As the positive valence of the element increases, its equivalent conductance in general decreases. Such elements as lead, tin, bismuth, antimony, arsenic and tellurium, which exhibit a great tendency to form complex anions, likewise exhibit a low value of the equivalent conductance. May we not conclude, therefore, that the less electropositive metallic elements are not homogeneous; that is, that the various atoms in these elements do not find themselves in the same condition in the liquid and possibly in the solid state.

#### VI. The Nature of Metallic Compounds of the Salt Type

Having shown that various metallic compounds dissolved in liquid ammonia are salt-like in character, we may extend the results obtained to compounds which are not soluble in this solvent. So far as the properties of these compounds are concerned, there is nothing to indicate that they differ materially from other compounds whose properties in solution have been studied. For example, there is nothing to indicate that the compounds of sodium with mercury differ materially from those of sodium with tin or lead.

One of the most remarkable facts in connection with intermetallic compounds is the multiplicity of compounds derivable from a given pair of metallic elements. This difficulty, which appears as an insurmountable obstacle to the extension of our valence conceptions to intermetallic compounds, is at once resolved when we take into account the great tendency of metallic elements to form complexes. The existence of complex metallic anions has been conclusively shown as a consequence of the results obtained in the study of solutions of metallic compounds in liquid ammonia. Whether complex cations may likewise exist is, at the present time, uncertain. It is possible, however, that such is the case. Furthermore, the data relative to the composition of metallic compounds are based largely on the properties of metals in the solid state; that is, on the melting-point diagrams. Compounds may appear in a solid state which have a relatively low stability in the liquid mixture; in other words, even very weak forces may lead to the formation of compounds in the solid state. So, for example, sodium and potassium form a compound NaK. Unquestionably this compound has a relatively low stability. At low concentrations such a compound might be expected to be completely dis-



sociated, in all likelihood, into atoms of sodium and of potassium. Dissolved in liquid ammonia, mixtures of sodium and potassium give no indications whatsoever of the existence of a compound.<sup>19</sup> It is probable that many of the compounds in which it would otherwise be necessary to assume a complex electropositive constituent are of this type; that is, they are relatively unstable complexes which are largely restricted to the solid state.

The physical properties of metallic compounds are in harmony with the theory of their constitution, as here outlined. The conductance of metallic compounds in the solid state is almost invariably lower than that of one of the constituents and is often lower than that of both constituents. This is the more true the more electropositive one constituent and the more electronegative the other. It may be inferred that the low conductance of intermetallic compounds of this type is due to the fact that many of the electrons are more or less bound up in the structure of the compound. The more electronegative elements in these compounds presumably bind, more or less firmly, a portion of the electrons available in such systems. In Table II are given values of the specific conductance of a number of metallic compounds. Following the formula of the compound at the head of each column, the values of the specific conductance multiplied by  $10^{-4}$  are given in order for the first element appearing in the formula of the compound, for the compound itself, and finally for the second element in the formula.

TABLE II  
SPECIFIC CONDUCTANCE OF METALLIC COMPOUNDS

Compound	Mg <sub>2</sub> Sn	MgCu <sub>2</sub>	Mg <sub>2</sub> Cu	MgZn <sub>2</sub>	Mg <sub>3</sub> Bi <sub>2</sub>	MgAl	Mg <sub>3</sub> Al <sub>2</sub>
	23.0	23.0	23.0	23.0	23.0	23.0	23.0
$\mu \times 10^{-4}$ .....	0.092	19.4	8.38	6.3	0.76	2.63	4.53
	8.60	64.1	64.1	17.4	0.84	35.1	35.1
Compound	MnAl <sub>3</sub>	FeAl <sub>3</sub>	NiAl <sub>3</sub>	Ag <sub>3</sub> Al <sub>2</sub>	Ag <sub>3</sub> Al	AgMg	AgMg <sub>3</sub>
	22.7	11.0	8.51	68.1	68.1	68.1	68.1
$\mu \times 10^{-4}$ .....	0.20	0.71	3.47	3.85	2.75	20.52	6.16
	35.1	35.1	35.1	35.1	35.1	23.0	23.0
Compound	Ag <sub>3</sub> Sb	Te <sub>2</sub> Sb <sub>2</sub>	TeSn	Te <sub>3</sub> Bi <sub>2</sub>	Cu <sub>2</sub> As		
	68.1	0.017	0.017	0.017	64.1		
$\mu \times 10^{-4}$ .....	0.93	0.48	0.97	0.045	1.70		
	2.56	2.56	8.60	0.84	2.85		

The low values of the conductance of magnesium stannide, Mg<sub>2</sub>Sn, and of the compounds of aluminum are particularly striking. Unless we assume that some of the electrons are bound within the structure of these compounds, it is difficult to account for the low value of the conductance of these substances.

<sup>19</sup> Kraus, *THIS JOURNAL*, **43**, 756 (1921).

In the case of compounds in which the more electronegative constituent is non-metallic in the elementary state, the conductance is often very low. In Table III are given values of the specific conductance of a number of compounds of this type. As may be seen from this table, the specific conductance of some compounds is very low while that of others is as high as that of some of the metallic elements.

TABLE III  
SPECIFIC CONDUCTANCE OF METALLIC COMPOUNDS<sup>20</sup>

Compound	CuS	PbO <sub>2</sub>	CdO	PbS	Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	Fe <sub>3</sub> O <sub>4</sub> <sup>b</sup>
$\mu \times 10^{-4}$ .....	0.85	0.43	0.083	0.042	2.3	0.0116
Compound	FeS <sub>2</sub> <sup>c</sup>	FeS <sub>2</sub> <sup>d</sup>	FeS <sup>e</sup>	Cu <sub>2</sub> O		
$\mu \times 10^{-4}$ .....	0.0042	0.060	0.22	0.025		

<sup>a</sup>  $\perp$  to axis.    <sup>b</sup> Magnetite.    <sup>c</sup> Pyrite.    <sup>d</sup> Marcasite.    <sup>e</sup>  $\perp$  C-axis.

It is clear that the property of metallicity is not confined to compounds of metals with other metallic elements. There is no substantial reason for believing that metallic oxides and sulfides differ essentially in their constitution from non-metallic oxides and sulfides. Since the latter substances are clearly salt-like in nature, it follows that the metallic condition of a substance does not preclude the possibility of a salt-like structure.

While many metallic compounds are differentiated from the elementary metals in the low value of their specific conductance, in other respects their properties correspond closely with those of elementary metals. For example, the temperature coefficient of the resistance of metallic compounds in the solid state is of the same order of magnitude as that of metallic elements under similar conditions. This would appear to indicate that the conductance change in such compounds is due, in all likelihood, to the increased resistance to motion, which conducting particles experience at higher temperatures, rather than to a decrease in the number of such particles. This statement, however, applies only to metallic compounds in which both constituents are relatively strongly electropositive. In compounds in which one of the constituents is strongly electronegative, the temperature-resistance curve often differs greatly from that for pure metals. In these compounds, at low temperatures, the resistance increases very largely with decreasing temperature, approximately as an exponential function of the temperature. At higher temperatures, the resistance passes through a minimum value, after which it increases more or less normally as a function of the temperature. It may be inferred that in these compounds at lower temperatures a portion of the electrons lose their freedom of motion entirely.

<sup>20</sup> Baedeker, "Die Elektrischen Erscheinungen in Metallischen Leitern," Vieweg, 1911, p. 31.

The mechanical properties of metallic compounds are likewise in agreement with the hypothesis that these compounds are in effect salts. Ductility is one of the characteristic properties of metallic elements. This property is almost entirely lacking in salts, which are invariably hard, brittle substances. Metallic compounds are as a rule hard and brittle.<sup>21</sup> The more electropositive one constituent and the more electronegative the other, the more do metallic compounds resemble salts in their mechanical properties. It is interesting to note that the strongly electronegative metallic elements are relatively hard and brittle in the pure state. This is what might be expected if these elements were compounds between positively and negatively charged atoms or atomic groups of the same element.

The value of the energy changes accompanying the formation of metallic compounds obviously has an important bearing on the theory of their constitution. While anything like complete data is lacking, such data as are available as well as qualitative observations support the view that the reactions involved in the formation of many metallic compounds are similar to those involved in the formation of salts.

TABLE IV  
HEATS OF FORMATION OF METALLIC COMPOUNDS IN KG. CAL.<sup>22</sup>

Compound	CuZn <sub>2</sub> <sup>23</sup>	MgZn <sub>2</sub>	Mg <sub>4</sub> Al <sub>3</sub>	CuAl <sub>2</sub>	CuZn <sub>10</sub>	CaZn <sub>4</sub>	Cu <sub>2</sub> Cd <sub>3</sub>
Heat per formula wt.	10.14	24.9	164.8	31.9	199.1	55.6	47.7
Compound	MgCd	NaCd <sub>2</sub>	NaCd	NaHg	NaHg <sub>2</sub>	NaHg <sub>4</sub>	KHg <sub>2</sub>
Heat per formula wt.	17.7	30.8	60.6	10.3	17.8	Ca.20	20
Compound	KHg <sub>3</sub>	NaI	Na <sub>2</sub> S	AgI	HgI	HgI <sub>2</sub>	PbS
Heat per formula wt.	Ca.33	69.1	89.3	13.8	14.2	25.2	20.3

In Table IV are given values for the heats of formation of a number of metallic compounds. The energy change accompanying the formation of the compound Mg<sub>4</sub>Al<sub>3</sub> is particularly striking, being approximately 40 Cal. per atom of Mg. This energy change is comparable with that accompanying the formation of many salts, as may be seen from the values given for salts in the table. Corresponding with the high heat of formation of the magnesium-aluminum compound, the electrical conductance of magnesium-aluminum alloys is low. It is well known that strongly electropositive metals combine with the more electronegative metals with great violence. The energy changes accompanying these reactions are certainly greater than those appearing in the above table. In metallic compounds, as in salts, the energy change is the greater the more electropositive one element and the more electronegative the other. For a given

<sup>21</sup> Desch, "Metallography," Longmans, Green and Company. 1910, p. 251.

<sup>22</sup> Roos, *Z. anorg. Chem.*, **94**, 354 (1916).

<sup>23</sup> Herschkowitsch, *Z. physik. Chem.*, **27**, 123 (1898).

electropositive element, the energy change accompanying reaction with another element diminishes as the second constituent becomes less electronegative. There is nothing to indicate that there is a sudden change in the energy effects as we pass from non-metallic to metallic compounds. In salt formation, the accompanying energy effect is largely due to the combination of the negative electron with the electronegative constituent to form an anion. The regularity of the energy effects accompanying the formation of metallic compounds indicates that a similar reaction takes place in the case of these substances. Naturally, the energy changes represent the integrated result of all the forces coming into play when a reaction occurs. Only a broad comparison of the energy relations in salts and metallic compounds has a significance.

### VII. Non-Saltlike Metallic Compounds

While many metallic compounds are of the nature of salts in which the more electropositive constituent is associated with a cation and the more electronegative constituent with an anion, there remains another class of compound metals, often containing non-metallic elements, which resemble the metallic elements in that the negative electrons are not associated with the electronegative elements present. Compounds of this type are sharply differentiated from compounds in which the negative electron is associated with an electronegative constituent, which compounds thus resemble the salts rather than the elementary metals.

The metallic properties of metallic elements are due to the negative electrons in the outer shell of the atom. Any atom which thus contains a negative electron not strongly united to its nucleus is metallic in the free state. In the presence of more strongly electronegative elements, these electrons unite with the electronegative atoms to form a stable complex, *i. e.*, an anion. The atom from which the electron is originally derived is thus electropositive, since it functions as a positively charged complex in the presence of electronegative elements. In the free state, the electropositive complex persists, the negative electrons in the body of the metal not being definitely joined to the atoms.

Many groups of elements exhibit decided electropositive properties in their compounds, and this is true not only of groups containing metallic elements but also of groups containing only non-metallic elements.

The attachment of an electron to the atomic nucleus in the case of non-metallic elements is greatly influenced by the presence of other atoms with which the first atom is combined. The presence of certain atomic groups tends to free the connection between the original atom and its associated electrons. In certain cases, a negative electron is in this manner freed from association with its atom and the resulting compound acquires metallic properties. The property of metallicity is, therefore, not an atomic

property in the sense that it is restricted to metallic elements and their compounds. The negative electron is the constituent to which metals owe their metallic properties and the rôle of the positive constituent is a secondary one.

It is well known that many groups of elements containing either non-metallic elements alone, or both metallic and non-metallic elements, function as stable electropositive ions in their compounds with electro-negative elements. The ammonium group and certain metal-organic groups are familiar examples of this type of positive ions. We should expect that if these groups could be obtained in the free state, the resulting compound would be metallic. Since these compounds contain electro-negative elements, it follows that such groups may prove to be unstable in the free state, for in the presence of negative electrons these elements tend to combine with them with the formation of new compounds. In case the group were stable, however, we should expect it to exhibit metallic properties.

This theory of the constitution of the electropositive groups is borne out by numerous observations. Thus, the ammonium group itself possesses sufficient stability to form an unstable amalgam. The properties of ammonium amalgams clearly indicate a measurable stability of the ammonium group.<sup>24</sup> The substituted ammonium groups, such as tetramethylammonium, possess a much greater stability than the ammonium group. These groups form relatively stable solid metallic compounds with mercury.<sup>25</sup> Even more remarkable are the properties of the tetra substituted ammonium groups in liquid ammonia solutions.<sup>26</sup> These groups may be reduced by electrolysis in ammonia solution. Under these conditions the groups dissolve in ammonia forming a characteristic blue solution which appears in every way identical with solutions of the alkali metals in the same solvent. That such groups are, in fact, typical metals is not to be doubted. Unfortunately, these groups are not sufficiently stable to permit of their being isolated. It is, however, apparent, from their properties in ammonia solution and in their compounds with mercury, that such groups, containing only non-metallic elements, are true metals resembling the alkali metals very closely.

Many metals form electropositive groups with organic radicals of the type  $R_{n-1}M^{n+}$ , where  $n$  is the normal valence of the element and  $R$  is an organic alkyl or aryl group. Compounds of the type  $R_{n-1}M^+X$ , where  $X$  is an anion, exhibit salt-like properties. In general, the smaller the value of  $n$ , the more salt-like is the resulting compound. Mercury salts of the type  $RHgX$  are exceptionally stable and by the electrolysis

<sup>24</sup> Coehn, *Z. anorg. Chem.*, **25**, 430 (1901).

<sup>25</sup> McCoy and Moore, *THIS JOURNAL*, **33**, 273 (1911).

<sup>26</sup> Palmaer, *Z. Elektrochem.*, **8**, 729 (1902). Kraus, *THIS JOURNAL*, **35**, 1732 (1913).

of these salts the free groups RHg have been obtained.<sup>27</sup> These groups in the free state are true metals. Even the group  $C_3H_7Hg$ , containing an enormous preponderance of non-metallic atoms, is a true metallic substance. These compounds are, therefore, to be classed with the metallic elements, since the negative electron is not associated with the less metallic elements present.

These free groups throw light on the question as to the source of the negative electrons to which metallic substances owe their metallic properties. The electrons concerned in metallic substances are the valence electrons, that is, the electrons to which chemical reactions are due.<sup>28</sup> Chemical reactions of this type consist essentially in a combination of the negative electron with an electronegative element or group of elements. If the source of electrons is a strongly electropositive element or group of elements and the electronegative constituent is strongly electronegative, then the resulting compound will be an electrolyte, *i. e.*, a salt. Non-salt-like substances are formed only when the negative electron remains associated with both the more electropositive and the more electronegative constituent. All the more electropositive elements thus form salts with strongly electronegative constituents. In salts of elements of high electropositive valence, however, the salt-like characteristics are greatly reduced, as for example, in stannic chloride.

On the other hand, it is not the non-metallic elements alone which possess the power of combining with negative electrons to form stable anions. This property is common to all but the most strongly electropositive metals. The resulting compounds, however, will exhibit metallic properties in the pure state in the case of the less electronegative elements, as a result of interaction between the charges at high concentrations.

Not all compounds, however, are to be ascribed primarily to the interaction of negative electrons. Other forces apparently come into play as a result of which combination occurs. The formation of complex anions is an example of this type. So little is known regarding these substances that it is not possible to venture a guess as to the nature of the mechanism involved in this type of combination.

Another class of metallic compounds in which the negative electron is not primarily concerned is found in the ammoniates of the metals of the alkaline earths. Here we have compounds of the type  $Ca(NH_3)_6$ .<sup>29</sup> These compounds appear to be metals whose properties closely resemble those of concentrated solutions of these metals in liquid ammonia. The fact that these compounds are metallic clearly indicates that the negative electrons are not primarily concerned in their constitution. It appears,

<sup>27</sup> Kraus, Ref. 26.

<sup>28</sup> Kraus, Ref. 26, p. 1741.

<sup>29</sup> Kraus, THIS JOURNAL, 30, 653 (1908). Biltz, *Z. anorg. Chem.*, 114, 241 (1920).

rather, that the group  $\text{Ca}(\text{NH}_3)_6^{++}$  is a strongly electropositive group of which  $\text{Ca}(\text{NH}_3)_6\text{Cl}_2$  is a salt. An important fact to be noted in this connection is that in the free group the ammonia molecules are similarly combined, *i. e.*, the group breaks down as a whole and not in stages when ammonia is withdrawn. The nature of the mechanism involved in the ammoniated metals, as in the ammoniated salts, remains to be disclosed.

### VIII. Summary

1. It is pointed out that the constitution of substances cannot be derived from their properties in a condensed state with any considerable degree of certainty. In order to determine the constitutions of metallic substances it is necessary to study their properties at low concentrations.

2. At low concentrations the elementary metals are salt-like substances, and it is suggested that metallic compounds will exhibit salt-like properties in even a more decided manner.

3. In solutions of metallic compounds in liquid ammonia, the more electronegative element functions as anion, as follows from the fact that it is precipitated on the anode on electrolysis. *All but the strongly electropositive elements exhibit a negative as well as a positive valence.*

4. The normal anions of metallic elements form complex anions in the presence of the element in question. These complex metallic compounds are similar to the complex iodides and sulfides which have been studied in aqueous solution. *The property of forming complex anions is one common to many metallic as well as non-metallic elements.*

5. It has been shown that the complex telluride ion carries two charges. In solution in ammonia the complex anions  $\text{TeTe}^{--}$  and  $\text{Te}_3\text{Te}^{--}$  exist. It may be inferred that the anions of the metals of the fifth group carry 3 and those of the fourth group 4 charges.

6. Since it has been shown that the metals selenium, tellurium, bismuth, antimony, arsenic, lead and tin form complex anions in ammonia solution, it may be inferred that other metals not soluble in ammonia form similar complex anions. *Metallic compounds of this class are, therefore, virtually salts.*

7. The multiplicity of compounds derivable from a given pair of metallic elements is accounted for on the hypothesis that in their compounds the more electronegative elements form complex anions. This brings metallic compounds into line with present conceptions of atomic structure.

8. The physical properties of metallic compounds are in harmony with the hypothesis that they possess a salt-like structure.

9. It is pointed out that the energy effect accompanying the formation of metallic compounds is of the same order of magnitude as that accompanying the formation of salts. As in the case of salts, the energy change

is the greater the more electronegative one element is with respect to the other.

10. Electropositive groups, such as the ammonium group, are virtually metals although their stability in the free state is not sufficient to permit their isolation in most instances. The most stable groups possess sufficient stability to demonstrate their metallic properties in the free state. Such groups resemble elements in their properties.

11. *The property of metallicity is not an atomic one.* It may be imparted to non-metallic elements by combination with other non-metallic elements. *The metallic state is due to the presence of uncombined negative electrons.*

12. The electrons which impart metallic properties to an element are those to which the chemical reactions of this element with other elements are due.

13. The reaction between strongly electropositive and strongly electronegative elements or groups of elements consists essentially in a combination of the negative electrons of the electropositive constituent with the atoms of the electronegative constituent.

14. In the metal ammoniates of the type  $\text{Ca}(\text{NH}_3)_6$ , which are metallic substances, the negative electrons are not primarily concerned.

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WORCESTER, MASSACHUSETTS

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## THE CRYSTAL STRUCTURES OF THE HEXAMMONIATES OF THE NICKEL HALIDES

BY RALPH W. G. WYCKOFF<sup>1</sup>

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**Introduction.**—When an excess of ammonium hydroxide is added to a solution of one of the nickel halides, small octahedral crystals are precipitated. These crystals have the composition  $\text{NiX}_2 \cdot 6\text{NH}_3$ , where X is chlorine, bromine or iodine.

Single crystals of considerable size can be grown by slow cooling from a not too strong solution. These are rarely perfect in internal structure and all of them are extremely fragile. Because of the ease with which

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