X-ray measurements are given for solid solutions of a number of binary systems of the alkali and ammonium halides.

It is concluded that for completely miscible systems, each solid solution behaves toward X-rays *as though it were a pure substance,* the reflecting power and volume of the new compound ion or atom being determined additively by the atomic numbers and volumes of the constituent atoms.

COLUMBUS, OHIO

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# THE REDUCTION OF METALS FROM THEIR SALTS BY MEANS OF OTHER METALS IN LIQUID AMMONIA SOLUTION

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## Mechanism of the Reduction Process

It is known that the alkali metals and the metals of the alkaline earths are soluble in liquid ammonia and ionize in solution with the formation of positive ions which are identical with the ions of the salts of the same metals in solution in the same solvent, and negative ions which consist of the negative electrons. If we reduce the salt $MX_m$ of a metallic element M whose positive valence is m, by means of another metal N of positive valence n, then the problem presented is similar to that of a solution of two salts without a common ion, the ionic constituents being $M^{m+}$, $N^{n+}$, $X^-$ and $e^-$.[1] We have, then the reaction equations,

$$MX_m = M^{m+} + mX^- \quad (a) \qquad Me_m = M^{m+} + me^- \quad (c)$$
$$NX_n = N^{n+} + nX^- \quad (b) \qquad Ne_n = N^{n+} + ne^- \quad (d)$$

Corresponding to these reaction equations we have the equilibrium equations,

$$(M^{m+})\,(X^-)^m = (K_1)\,(MX_m) \quad (1) \qquad (M^{m+})\,(e^-)^m = (K_3)\,(Me_m) \quad (3)$$
$$(N^{n+})\,(X^-)^n = (K_2)\,(NX_n) \quad (2) \qquad (N^{n+})\,(e^-)^n = (K_4)\,(Ne_n) \quad (4)$$

Here $K_1$, $K_2$, $K_3$, $K_4$ represent the mass-action functions of the reactions in question. They will have definite values for definite conditions of the system, but will vary as a function of the concentration of the various constituents present, approaching definite limiting values at low concentrations. The reaction taking place in the solution will depend upon the values of the mass-action functions and the solubilities of the constituents $MX_m$, $NX_n$, $Me_m$ and $Ne_n$. We may distinguish a number of different cases, depending upon the relative values of the mass-action functions and the solubilities of the various constituents.

*(1) The mass-action functions have approximately the same value for all constituents and the solubility of these constituents is high and of the same order of magnitude.* In this case interaction will take place between the salt $MX_m$ and the reducing metal $Ne_n$ but, because of the high value

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[1] For the sake of simplicity we may assume that the negative ions are univalent.

of the solubility of the products of metathesis, precipitation will not occur. The solution, however, will contain both the salts $MX_m$ and $NX_n$ and the neutral metal atoms $Me_m$ and $Ne_n$. The extent to which metathesis occurs will depend upon the relative values of the mass-action functions under the conditions of the system. An example of a system of this type is found in a solution of sodium iodide to which metallic potassium has been added. Here metathesis takes place with the formation of potassium iodide and metallic sodium, but potassium iodide is not precipitated except at very high concentrations, owing to its high solubility.[2]

(*2*) *The mass-action functions are of the same order of magnitude, but the solubility product of the constituent $NX_n$ is low.* In this case metathesis takes place with the precipitation of the salt $NX_n$, while the solution contains an equivalent amount of the metal $Me_m$. The completeness of precipitation depends upon the solubility of the salt $NX_n$. An example of a reaction of this type is found in a solution of potassium amide to which metallic sodium has been added. Sodium amide is much less soluble than potassium amide and accordingly precipitates, leaving behind metallic potassium. In this case, however, precipitation is incomplete because of the measurable solubility of sodium amide. A more striking example is found in the case of solutions of potassium halides, to which metallic calcium has been added. The calcium halides are relatively difficultly soluble in liquid ammonia and practically complete precipitation of calcium takes place, while the potassium thus reduced remains behind in the solution. The ionic reaction may be represented by the equation: $Ca^{++} + 2Cl^- = CaCl_2$.

(*3*) *The solubility product of the reducing metal $Ne_n$ is low, while the solubility product of the salt $NX_n$ is likewise low.* Even though the solubility product of the metal $Ne_n$ is relatively low, which corresponds in general to the case of a weakly electropositive metal, reduction may nevertheless be effected if the solubility product of the salt $NX_n$ is sufficiently low. An example of a reaction of this type is found in the reduction of sodium salts by means of magnesium. Magnesium is only slightly soluble in liquid ammonia, giving a transparent blue solution. When sodium bromide is treated with metallic magnesium, reduction takes place because of the low solubility of magnesium bromide, metallic sodium remaining in solution. An equilibrium must finally exist in the solution among the various constituents, the concentrations being dependent upon the solubility of magnesium and of magnesium bromide.

[2] It is of interest to point out that the amount of free metal in solution cannot be specified in terms of the positive constituents. Both positive constituents may be present chiefly as positive ions which are similarly related to the negative ions present. The amount of free metal is determined by the uncombined negative electrons whether free or in association with positive ions.

(4) *The solubility product of the reducing metal* $Ne_n$ *is very low and the ions* $X^-$ *are removed from solution by interaction of the ions* $M^{m+}$ *with the salt* $NX_n$. If the ions $X^-$, together with ions $N^{n+}$ of the reducing metal, can be removed from solution by interaction with the metallic ions $Me^{m+}$, then there will be left behind in the solution free metal $Me_m$. If the solubility product of the reducing metal is low, the concentration of the ions $N^{n+}$ in equilibrium with other constituents must be correspondingly low, in order that reduction may occur. It is necessary, in other words, that a new type of compound should be formed which does not yield the ions $N^{n+}$. The reaction may be illustrated by the reduction of potassium amide by means of metallic aluminum. In this case the reaction (b) may be written,

$$Al^{+++} + 3NH_2^- = Al(NH_2)_3 \qquad \text{(e)}$$

Aluminum amide is doubtless an exceedingly weak base and the concentration of aluminum ions in equilibrium with the undissociated aluminum amide and $NH_2^-$ ions present in solution, due to the original potassium amide, is exceedingly low. However, aluminum amide is an amphoteric base, so that a secondary reaction occurs as follows,

$$Al(NH_2)_3 + KNH_2 = Al(NH_2)_2.NHK.NH_3 \qquad \text{(f)}$$

It is evident that the aluminum ions, as rapidly as they go into solution, are removed according to Reaction e, in which the amide is formed. But the concentration of the aluminum ions is still further lowered as a result of the amphoteric properties of aluminum amide, whereby potassium ammono-aluminate is formed. It is obvious that the concentration of aluminum ions, due to the potassium ammono-aluminate, must be exceedingly low. In general, it may be expected that, in the reduction of the metallic amides by means of less electropositive metals, interaction between the amide of the reducing metal and the amide originally introduced will occur, inasmuch as it has been shown that even the amides of the alkali metals exhibit amphoteric properties or, at any rate, form definite compounds. The above type of reaction suggests a mechanism for the action of strong bases on such elements as aluminum and zinc in aqueous solution.[3]

(5) *The reduced metal* $Me_m$ *has a low value of the solubility product and is not capable of existing as anion.* In this case reaction between the salt $MX_m$ and the reducing metal $Ne_n$ is one of simple metathesis according to the equation,

$$M^{m+} + me^- = Me_m \qquad \text{(g)}$$

and we have the corresponding equilibrium equation,

$$(M^{m+})\ (e^-)^m = K_5(Me_m) \qquad (5)$$

$(M^{m+})\ (e^-)^m$ is the positive solubility product of the metal and $Me_m$

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[3] Observations by Dr. F. W. Bergstrom. These reactions will be discussed in detail by Dr. Bergstrom in a forthcoming publication.

is the concentration of neutral metal in solution in equilibrium with free metal. The completeness of the precipitation depends upon the value of the solubility product of the metal $Me_m$. For the less electropositive metals this value is extremely low and such metals, therefore, are completely precipitated from solution by means of more electropositive metals, whose solubility product is relatively high. The reduction of silver salts by means of sodium in liquid ammonia is a typical example of a reaction of this type, since silver is only weakly electropositive and does not form a compound with sodium. We have here the reaction, $Ag^+ + e^- = Ag\,e$. Other metals, which are similarly incapable of forming compounds with the reducing metal, are precipitated in the free metallic state.

(6) *The reduced metal is capable of forming a stable anion with the negative electron.* If M is the metal to be reduced, of positive valence $m^+$ and of negative valence $\mu^-$, then there will exist in solution the equilibrium reaction,

$$Me_m + \mu e^- = Me_m e^-_\mu \qquad \text{(h)}$$

where $Me_m$ represents the neutral metal of normal positive valence m and $Me_m e^-_\mu$ represents an anion of the same metal of normal negative valence $\mu$.[4] Corresponding to Reaction h, we have the equilibrium equation,

$$(Me_m)\,(e^-)^\mu = K_6(Me_m e^-_\mu) \qquad (6)$$

$Me_m$ may be termed the solubility ratio of the metal in the electronegative condition. It is the concentration of neutral metal atoms in solution in equilibrium with negative electrons. The negative solubility ratio of a metal may be expected to have a very low value in the case of the more electropositive metals and a relatively high value in the case of the more electronegative elements. It may be pointed out, however, that even in the case of such elements as tellurium and sulfur, this solubility ratio does not have a very high value. On the other hand, the value is comparatively high in the case of iodine.

The positive and negative ion-products of the elements would appear to correspond approximately with the position of the positive and negative elements in the electromotive-force series. The single electrode potentials, however, serve to give only a rough measure of the solubility products, in view of the fact that the molecular conditions of the solutions in question are not strictly comparable.

In the reduction of the more electronegative elements which have marked amphoteric properties, reduction by means of more electropositive elements leads not to the precipitation of the free metal but rather to the precipitation of a compound of this metal with a more electropositive element, the less electropositive metal acting as anion.

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[4] In general all the metals which occupy an intermediate position in the potential series exhibit amphoteric properties; that is, they act as anions as well as cations, depending on conditions.

An example of a reaction of this type is found in the reduction of antimony by means of metallic sodium. The ionic reaction in this case is expressed by the following equation: $Sb^{+++} + 6e^- = Sbe_3e^-_3$. Whether or not the complex anion will remain in solution depends upon the solubility product of the compound formed in the reaction,

$$Me_me^-_\mu + \mu N^+ = Me_mNe_\mu \qquad \text{(i)}$$

the reducing metal N being assumed to be univalent. As a rule, compounds of simple anions of the type $Me_me^-_\mu$ have a low solubility and are precipitated from solution. The more electronegative the element, the higher, in general, is the solubility of the compound.

(7) *The reduced metal forms a complex anion.* In many cases the anion $Me_me^-_\mu$ is capable of reacting with additional atoms of the metal M to form a complex anion. This reaction may be expressed by the equation,

$$Me_me^-_\mu + xMe_m = (Me_m)_{x+1}\,e^-_\mu \qquad \text{(j)}$$

This anion will be in equilibrium with the ions $N^+$ of the reducing metal, according to the equation,

$$(Me_m)_{x+1}\,e^-_\mu + \mu N^+ = (Me_m)_{x+1}\,(Ne)_\mu \qquad \text{(k)}$$

As a rule, the salts of complex anions are much more soluble than are the normal salts. Numerous examples of this case exist, such as lead, antimony, bismuth, etc. In the case of the polyiodides, it has been found that the more complex iodides exhibit a higher solubility in non-aqueous solvents than do the simpler iodides. The number of atoms x of the metal, combined with the original anion in the complex anions, varies, in general, as a function of conditions.

In some instances, the salts of more complex anions are more stable than those of less complex ones. In such cases a reaction of the following type takes place,

$$r(Me_m)_{x+1}\,e^-_\mu = s(Me_m)_{x+y+1}\,e^-_\mu + \mu(r - s)e^- \qquad \text{(l)}$$

where $r(x+1) = s(x+y+1)$. In this case the less complex anion breaks down in solution to form a more complex anion and free electrons. The free electrons, together with the ions $N^{n+}$ of the reducing metal, thus constitute free metal in solution. Examples of reactions of this kind are found in the stannides and plumbides of the alkali metals. If compounds rich in sodium are dissolved in liquid ammonia, free metallic sodium is formed, together with a compound richer in the more electronegative element, which remains in solution.

In some instances reactions of this type take place in the case of compounds which are not soluble in liquid ammonia, notably in the case of the hydrargides. Thus the compound $Na_2Hg_2$, which is insoluble, breaks down in the presence of ammonia according to the equation, $2Na_2Hg_2 = Na_2Hg_4 + 2Na$; the compound $Na_2Hg_4$ being insoluble in liquid ammonia remains as solid, while the sodium which is formed as a result of this reaction dissolves in liquid ammonia, where its presence is readily recognized as a result of its characteristic blue color.

If we treat the compound $\mathrm{Me_mNe_\mu}$ with a salt $\mathrm{MY_m}$ we have a reaction, $\mathrm{mMe_me^-{}_\mu} + \mu\mathrm{M^{m+}} = \mathrm{(Me)_m(Me)_\mu} = \mathrm{M_{m+\mu}}$. The product $\mathrm{(Me_me^-{}_\mu)^m}$ $\mathrm{x(M^{m+})^\mu}$ is the solubility product of the metal. This reaction may be illustrated by the action of lead nitrate on the plumbide $\mathrm{Na_4Pb_9}$, thus: $\mathrm{Pb_9{}^{----}} + \mathrm{2Pb^{++}} = \mathrm{Pb_2Pb_9}$, metallic lead being precipitated.

## Experimental Part

A detailed description of the apparatus employed in effecting the reduction of various salts may be omitted. The reactions were carried out in a cylindrical glass tube immersed in a bath of boiling ammonia. To the bottom of the reaction tube was sealed a smaller tube through which pure ammonia in the form of vapor was introduced and condensed under pressure of about 20 cm. of mercury. The contents of the reaction tube were stirred by introducing ammonia vapor through this tube. The reducing metal and the salt to be reduced were introduced through the top of the reaction tube, which was closed by means of a rubber stopper.

The reaction may depend upon whether sodium or salt is present in excess. In most instances the reducing metal was first introduced and then salt added until the blue color, characteristic of the presence of free metal, disappeared. In the case of metals that yield soluble anions, which are generally highly colored, an exact end-point could not be determined.

Preliminary measurements were usually carried out, in which weighed amounts of salt were gradually added until the color was discharged. This procedure is not very accurate because of the fact that sufficient impurities are introduced in this process to react with appreciable amounts of the reducing metal. To avoid this difficulty, the end-points were finally checked by adding at one time a sufficient quantity of salt to approach the end-point very nearly. Since the amount of the reacting materials was necessarily small, a high degree of precision was not obtained from these experiments. Nevertheless, it was possible to determine the atomic ratios of the reacting substances.

**Reduction of Mercury Salts by Means of Sodium.**—According to Joannis,[5] on treating mercury with a concentrated solution of sodium, a compound is formed whose composition corresponds to the formula $\mathrm{NaHg_8}$. Schüller[6] in his melting-point determinations has shown the existence of compounds corresponding to the formulas $\mathrm{Na_3Hg}$, $\mathrm{Na_5Hg_2}$, $\mathrm{Na_3Hg_2}$, $\mathrm{NaHg}$, $\mathrm{NaHg_2}$ and $\mathrm{NaHg_4}$.

Experiments were carried out with mercuric iodide, mercuric cyanide

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[5] Joannis, *Compt. rend.*, **113**, 795 (1891).

[6] Schüller, *Z. anorg. Chem.*, **40**, 389 (1904).

and mercurous iodide. The results in the cases of these three salts were substantially the same. When a mercurous salt is added to a sodium solution, immediate reaction occurs with the precipitation of finely divided metal. Assuming that the anion of the mercury salt combines with sodium to form the corresponding sodium salt, the ratio of sodium to mercury atoms in the precipitate initially formed was found to be very nearly unity. On standing, however, the supernatant liquid, which was originally colorless, gradually turned blue, finally becoming quite opaque. On again adding a suitable amount of salt, the color was discharged, but returned on standing. This process was repeated a number of times. Apparently, the compound initially precipitated has a composition corresponding to the formula NaHg. This compound, however, is unstable in the presence of ammonia, breaking down to a compound richer in mercury, which is insoluble in ammonia, as are all the metallic mercury compounds, and free sodium, which is soluble in ammonia. By increasing the amount of salt initially added, it was found that when a permanently colorless solution is formed, the composition of the precipitate corresponded to the formula $NaHg_2$.

The results of a number of determinations are given in Table I, in which the number of the experiment is given in the first column, the weight of sodium in the second column, the weight of mercuric cyanide in the third column and in the last column the ratio of sodium to mercury in the precipitated compound, assuming that reaction takes place according to the equation, $(2 + x)Na + Hg(CN)_2 = 2NaCN + Na_xHg$.

Table I

Reduction Data, Mercury

| Expt. | Na | $Hg(CN)_2$ | Na/Hg |
|---|---|---|---|
| 1[a] | 0.1998 | 0.7320 | 0.998 |
| 2[b] | .1998 | .8146 | .695 |
| 3[c] | .0989 | .3841 | .830 |
| 4[d] | .0989 | .3948 | .75 |
| 5[e] | 0.1240 | 0.4950 | 0.75 |
| 6[f] | .1400 | .5985 | .568 |
| 7[g] | .1186 | .5220 | .497 |

[a] Solution transparent through main tube. [b] Blue color returned on standing. [c] Solution just transparent through main tube. [d] Solution initially very nearly colorless. [e] Solution at first transparent through main tube; color intensifies on standing. [f] Solution readily transparent through main tube; little change on standing. [g] Solution immediately and permanently decolorized.

As may be seen from Expt. 7 the color was almost completely discharged when the amount of sodium to mercury corresponded to the formula NaHg. On the other hand, as in the case of Expts. 2 and 5, the solution did not remain colorless after initial precipitation, even when the ratio of sodium to mercury was as low as 0.695. As may be seen from Expt. 7, precipitation was complete and the solution remained permanently colorless when the ratio of sodium to mercury in the compound was 0.497. It is evident that an initial precipitate is formed, of composition corresponding to NaHg, and that this compound is unstable in the presence of ammonia, while with larger quantities of mercuric cyanide a compound corresponding to the formula $NaHg_2$ is precipitated, which is stable in the presence of ammonia. In order to check the behavior of the compound NaHg, the same compound was formed by the direct union of the elements in equal atomic proportions in a vacuum. The resulting compound was then treated with liquid ammonia. After a few hours an opaque blue solution was formed, indicating the presence of free metallic sodium. It appears that the original compound breaks down according to the equation, $2NaHg = Na + NaHg_2$. There must be an equilibrium between the compounds $NaHg_2$, NaHg and a solution of sodium in ammonia at some definite concentration. This concentration must be quite high, since in Expt. 6 a permanent blue color was obtained with a ratio of sodium to mercury equal to 0.568.

**Reduction of Cadmium Salts by Sodium.**—Mathewson,[7] by the method of thermal analysis, obtained the compounds $NaCd_2$ and $NaCd_5$. With both cadmium iodide and cadmium cyanide in liquid ammonia solution, difficulty was experienced in obtaining a satisfactory end-point, chiefly because of the low solubility of these salts. The ratio Na/Cd found for the precipitate varied from 0.2 to 1.0, many of the values lying in the neighborhood of 0.5. In many instances unchanged salt was found with the precipitated metal at the end of the reaction. It is probable that the higher values of the ratio Na/Cd are more nearly correct and it is not improbable that a compound NaCd is formed. The precipitate is reactive toward water and air.

**Reduction of Zinc Salts by Sodium.**—Both zinc iodide and zinc cyanide are readily reduced by means of sodium in liquid ammonia. The cyanide is preferably used because of the absence of hygroscopic properties. Reaction occurs immediately on addition of the zinc salt, a finely divided metallic precipitate being formed which is extremely reactive both with respect to water and air.

Some of the results are given in Table II.

TABLE II

REDUCTION DATA, ZINC

| Expt. | Na | $Zn(CN)_2$ | Na/Zn |
|---|---|---|---|
| 1[a] | 0.1658 | 0.3555 | 0.38 |
| 2[b] | .1243 | .2763 | .296 |
| 3[c] | .0887 | .2022 | .24 |
| 4[d] | .0773 | .1764 | .234 |
| 5[e] | .1458 | .3253 | .289 |

[a] Solution just transparent through small tube but opaque through main tube.
[b] Solution readily transparent through small tube and light blue through main tube.
[c] Solution just colorless. [d] Solution colorless. [e] Solution nearly colorless.

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[7] Mathewson, *Z. anorg. Chem.*, **50,** 182 (1906).

It is evident that a compound is formed for which the ratio Na/Zn lies between 0.24 and 0.289. This indicates a compound of composition corresponding to the formula $NaZn_4$. This compound is much richer in sodium than $NaZn_{12}$ obtained by Mathewson[8] by the method of thermal analysis.

**Reduction of Tin Salts by Sodium.**—By the method of thermal analysis Mathewson[9] has identified the compounds $Na_4Sn$, $Na_2Sn$, $Na_4Sn_3$, NaSn and $NaSn_2$. According to observations by one of the present writers,[10] the alkali metals react directly with metallic tin in liquid ammonia solution. Reaction takes place somewhat slowly, the blue color characteristic of the alkali metal gradually passing from blue to greenish-yellow, and finally to a transparent red. The greenish-yellow color is, without doubt, due to a mixture of various constituents present in the solution including, perhaps, free sodium.

On treating a tin salt, such as stannous iodide, with metallic sodium, a similar series of color changes takes place. It was found difficult to fix precisely the transition from blue to red, so that it was not possible to determine the point at which free sodium disappears. On adding pellets of stannous iodide until a change from green to red occurred, the ratio Na/Sn for the compound was found to have a value of 3.8, which corresponds approximately with that of a compound of the formula $Na_4Sn$.

A number of determinations were carried out, the results of which are given in Table III.

TABLE III

REDUCTION DATA, TIN

| Expt. | Na | $SnI_2$ | Na/Sn | Expt. | Na | $SnI_2$ | Na/Sn |
|---|---|---|---|---|---|---|---|
| 1[a] | 0.1072 | 0.2526 | 4.87 | 5[e] | 0.1045 | 0.2889 | 3.87 |
| 2[b] | .0623 | .1596 | 4.34 | 6[f] | .1045 | .3027 | 3.62 |
| 3[c] | .0912 | .2453 | 4.03 | 7[g] | .1072 | .3170 | 3.492 |
| 4[d] | .1045 | .2821 | 4.03 | | | | |

[a] Solution greenish-yellow. [b] Solution still green. [c] Solution less green, with slightly brownish tint. [d] Solution still retains greenish tint. [e] Solution slightly green. [f] Opaque orange-red solution. [g] Dark red solution, transparent through small tube.

On adding an excess of stannous iodide, the red color is at first intensified, after which precipitation of metallic tin occurs until the solution becomes colorless. This stage of the reaction takes place according to the equation, $2NaSn_x + SnI_2 = 2NaI + Sn.Sn_x$. A definite color change from blue to red obviously does not occur and it may be inferred that the valence compound $Na_4Sn$ is not stable in solution but breaks down into free sodium and a compound richer in tin. In this case complete disappearance of sodium in the solution will not occur until the

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[8] Mathewson, *Z. anorg. Chem.*, **48**, 196 (1906).

[9] Mathewson, *ibid.*, **46**, 101 (1905).

[10] Kraus, unpublished observations.

amount of tin added is in excess of that corresponding to the formula $Na_4Sn$. This question will be discussed somewhat further in connection with the reduction of lead salts.

**Reduction of Lead Salts by Sodium.**—Mathewson[11] by the method of thermal analysis has identified the compounds $Na_4Pb$, $Na_2Pb$, NaPb, and $Na_2Pb_5$. More recently Calingaert and Boesch[12] identified the compound $Na_5Pb_2$. Joannis[13] by the direct action of the elements in liquid ammonia solution claims to have obtained the compounds $Na_2Pb$ and $NaPb_2$.

When a stick of lead is suspended in a solution of sodium in ammonia, a fairly rapid reaction takes place, the characteristic blue color changing to an opaque, dark green. There is apparently no transition point from blue to green. A certain amount of metallic precipitate is also formed in this process. It would seem that this precipitate is a compound of intermediate composition. According to Posnjak and Smyth,[14] a solution of a sodium-lead compound in equilibrium with lead contains approximately 2.25 atoms of lead per atom of sodium.

On adding lead iodide to a solution of sodium in liquid ammonia, the blue color gradually disappears and a green color takes its place. The transition from blue to green is not sharp. The more concentrated solutions of the compounds of sodium and lead are quite opaque.

It appears probable that on the addition of a lead salt to sodium in liquid ammonia reaction occurs with the initial formation of the normal plumbide $Na_4Pb$. This compound, however, is unstable, decomposing to free sodium and a compound richer in lead. All the sodium in solution, therefore, should not disappear until the relative amount of lead is much greater than corresponds to the ratio $Na/Pb = 4$. To test this, alloys of sodium and lead of various composition were made up and treated with liquid ammonia. An alloy corresponding to the composition NaPb dissolved quite readily in liquid ammonia at its boiling point, giving a green solution. An alloy corresponding to the composition $NaPb_2$ was likewise soluble and the solution was green, but was much darker than in the case of the compound NaPb. An alloy corresponding to the composition $Na_2Pb$ dissolved slightly in liquid ammonia, yielding a yellowish-green solution.

To establish the nature of these solutions further, rough conductance measurements were carried out with solutions of lead alloys in liquid ammonia. Potassium was used in preference to sodium, since the reaction with potassium takes place more readily than with sodium. A

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[11] Ref. 7, p. 175.

[12] Calingaert and Boesch, THIS JOURNAL, **45**, 1901 (1923).

[13] Joannis, *Compt. rend.*, **113**, 745 (1891); **114**, 585 (1892).

[14] Smyth, THIS JOURNAL, **39**, 1299 (1917).

weighed amount of potassium was added to liquid ammonia, together with various amounts of lead filings, and the solution was stirred until no further reaction occurred, after which the conductance was measured.

The results are given in Table IV, in which the dilution in liters per atom of sodium is given in the first column, the weight of lead added in the second column, the mean composition of the solution in the third column, and the equivalent conductance in the last column.

TABLE IV

CONDUCTANCE OF SOLUTIONS OF POTASSIUM IN AMMONIA AFTER REACTION WITH VARIOUS AMOUNTS OF LEAD

Weight of potassium, 0.1028; cell constant, 1.74

| Diln. in liters per atom of Na | Lead added G. | Compn. | Equiv. cond. |
|---|---|---|---|
| 13.3 | 0.1361 | $K_4Pb$ | 330 |
| 13.3 | .0688 | $K_4Pb_{1.5}$ | 238.5 |
| 14.45 | .1353 | $K_4Pb_{2.5}$ | 179.6 |
| 15.97 | .2041 | KPb | 99.2 |
| 15.97 | .545 | $KPb_2$ | 46.3 |
| 17.12 | large excess | $KPb_{2.25}$ | 21.3 |

After standing overnight a portion of the ammonia in the solution had evaporated and the equivalent conductance was found to be 15.7 at a dilution of approximately 7.5 liters. The equivalent conductance of potassium nitrate at a dilution of 15.85 liters is 92.9,[15] while that of metallic potassium at a dilution of 15.87 liters is 532.1.[16] It is not to be expected that the equivalent conductance of a potassium plumbide, whatever its complexity may be, will be greater than that of a normal electrolyte, such as potassium nitrate. The high values of the equivalent conductance of the solutions up to a composition corresponding to KPb must be due to the presence of free metallic sodium in these solutions. The phenomenon is similar to that observed in the case of mercury, with the exception that while the hydrargides are insoluble in liquid ammonia the corresponding plumbides are soluble.

**Reduction of Antimony and Bismuth Salts by Sodium.**—Mathewson[17] has identified the compounds $Na_3Sb$ and NaSb from the melting point diagram and also the corresponding compounds $Na_3Bi$ and NaBi. Joannis[13] has obtained the compounds $Na_3Sb$ and $Na_3Bi$ by the action of sodium in liquid ammonia on the metals. Peck[18] has shown that the ratio of sodium to antimony in equilibrium with free antimony varies as a function of concentration, approaching a maximum value corresponding to $Na_3Sb_7$.

Using antimony tribromide and bismuth trichloride as salts, satisfac-

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[15] Franklin and Kraus, THIS JOURNAL, **27**, 199 (1905).

[16] Kraus, *ibid.*, **43**, 755 (1921).

[17] Ref. 7, p. 194.

[18] Peck, THIS JOURNAL, **40**, 339 (1918).

tory end-points were not obtained. Only preliminary measurements were carried out with materials which may not have been entirely free from moisture. The ratio Na/Sb was found to lie at approximately 4.8, while the corresponding ratio in the case of bismuth was found to be 3.3. Doubtless both these values are too high.

**Reduction of Thallium by Sodium.**—According to the melting-point diagram, the compounds NaTl, $Na_2Tl$ and $Na_5Tl$ exist.[19] In the present investigation the action of thallous iodide on solutions of sodium in ammonia was investigated. Reaction takes place immediately with the formation of a metallic precipitate, the blue color disappearing and a greenish-yellow solution being formed. The residual color of the final solution indicates the formation of a compound slightly soluble in ammonia. This is indicated by the fact that on the addition of ammonium chloride the color is discharged. On allowing the solution to stand for a few minutes, however, the color was found to return. It is scarcely possible that the color can be due to the presence of impurities, such as lead or other metals, since no tests for such metals could be obtained. Moreover, if the result were due to the presence of a soluble compound of an electronegative metal as impurity, the color would not return after the addition of ammonium chloride. The precipitated compound is highly reactive toward both air and water.

The results of a number of determinations of its composition are given in Table V, assuming that reaction takes place according to the equation, $(1 + x)Na + TlI = NaI + Na_xTl$.

TABLE V

REDUCTION DATA, THALLIUM

| Expt. | Na | TlI | Na/Tl |
|---|---|---|---|
| 1[a] | 0.0893 | 0.5747 | 1.23 |
| 2[b] | .084 | .4839 | 1.5 |
| 3[c] | .075 | .4341 | 1.49 |

[a] Too much salt added. [b] Near end-point; solution slightly green. [c] Solution very slightly green.

The ratio Na/Tl evidently has a value of 1.5, which corresponds to a compound of the formula $Na_3Tl_2$. This compound does not appear in the melting-point diagram.

**Reduction of Silver by Sodium.**—So far as is known, silver and sodium form no compounds. Silver cyanide and silver iodide were added to solutions of sodium in liquid ammonia; a metallic precipitate was immediately formed which was inactive, both with respect to air and water. Several determinations of the ratio Na/Ag gave values of 0.10 and 0.09, which indicates that a compound is not formed between sodium and silver in the process of reduction.

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[19] Kurnakow and Puschin, *Z. anorg. Chem.*, **30**, 93 (1902).

**Reduction of Silver by Calcium.**—According to the melting-point diagram, calcium and silver form the compounds $CaAg_4$, $CaAg_3$, $CaAg_2$, and perhaps $Ca_2Ag$.[20] On reduction of silver cyanide, a metallic compound is precipitated which is markedly reactive toward water, but not very reactive toward air.

The ratio Ca/Ag was determined and the results are given in Table VI.

TABLE VI

REDUCTION DATA, SILVER

| No. | Ca | AgCN | Ca/Ag |
|---|---|---|---|
| 1[a] | 0.085 | 0.179 | 1.085 |
| 2[b] | .0512 | .112 | 1.032 |

[a] Solution nearly colorless. [b] Solution very nearly colorless.

It is evident that a compound of composition corresponding to the formula CaAg is formed. This compound does not appear among those previously given in the literature.

**Reduction of Zinc by Calcium.**—According to the method of thermal analysis, calcium and zinc form the compounds $CaZn_{12}$, $CaZn_4$, $Ca_2Zn_3$, $Ca_4Zn$ and perhaps CaZn.[21] On reducing zinc cyanide, a metallic precipitate is formed, the solution becoming colorless. This precipitate was found to be very reactive toward water and air, but less so than the sodium compound. The ratio Ca/Zn was calculated from the weights of materials employed.

The results are given in Table VII.

TABLE VII

REDUCTION DATA, ZINC

| No. | Ca | $Zn(CN)_2$ | Ca/Zn |
|---|---|---|---|
| 1[a] | 0.0842 | 0.032 | 6.72 |
| 2[b] | .0744 | .027 | 7.0 |

[a] Solution colorless. [b] Solution slightly blue.

The ratio corresponds to a compound of composition $Ca_7Zn$, a compound much richer in calcium than any found by the method of thermal analysis.

**Reduction of Mercury Salts by Calcium.**—Alloys of calcium and mercury have not been fully investigated by the method of thermal analysis, the compound $CaHg_4$ having been shown to exist.[22] Schürger[23] records the compound $CaHg_5$, Férée[24] $Ca_3Hg_4$, and Moissan and Chavanne[25] describe $CaHg_2$. On reducing mercuric cyanide by means of metallic calcium, a fine, gray, metallic precipitate is formed, while the solution

[20] Baar, *Z. anorg. Chem.*, **70,** 385 (1911).

[21] Donski, *ibid.*, **57,** 189 (1908).

[22] Cambi and Speroni, *Atti accad. Lincei*, **23,** II, 599 (1914).

[23] Schürger, *Z. anorg. Chem.*, **25,** 426 (1900).

[24] Férée, *Compt. rend.*, **127,** 619 (1898).

[25] Moissan and Chavanne, *ibid.*, **140,** 125 (1905).

becomes colorless. This precipitate was found to be very reactive toward water and air. Mercuric iodide was similarly reduced.

Some of the results are given in Table VIII.

TABLE VIII

REDUCTION DATA, MERCURY

| Expt. | Ca | $Hg(CN)_2$ | Ca/Hg |
|---|---|---|---|
| 1[a] | 0.1605 | 0.4042 | 1.5 |
| 2[b] | .1270 | .3489 | 1.296 |
| 3[c] | .0732 | .1711 | 1.7 |
| | | $HgI_2$ | |
| 4[d] | 0.1341 | 0.6070 | 1.506 |
| 5[e] | .1323 | .6504 | 1.309 |
| 6[f] | .0782 | .3572 | 1.49 |

[a] Very near end-point. [b] Past end-point. [c] Opaque blue solution. [d] Solution slightly blue. [e] Past end-point. [f] Solution very slightly blue.

These experiments yield a value 1.5 for the ratio Ca/Hg, corresponding to a compound of the formula $Ca_3Hg_2$. A compound of this composition has not hitherto been obtained.

**Reduction of Lead Salts by Calcium.**—By the method of thermal analysis, the compounds $CaPb_3$, CaPb and $Ca_2Pb$ have been identified.[26] On adding plumbous iodide to a solution of calcium in liquid ammonia a black precipitate is formed, while the solution becomes colorless. This precipitate is found to be quite reactive toward water, but not especially so toward air.

The results of a number of experiments are given in Table IX.

TABLE IX

REDUCTION DATA, LEAD

| Expt. | Ca | $PbI_2$ | Ca/Pb |
|---|---|---|---|
| 1[a] | 0.0733 | 0.5142 | 0.640 |
| 2[b] | .0888 | .6224 | .641 |
| 3[c] | .0598 | .4060 | .694 |
| 4[d] | .0598 | .4216 | .633 |

[a] Colorless in side tube; slightly blue in large tube. [b] Color discharged. [c] Transparent through side tube; opaque through main tube. [d] Very pale blue in main tube.

The value obtained for the ratio Ca/Pb lies very near to 0.667, which corresponds to a compound of formula $Ca_2Pb_3$. This compound is not found in the literature.

**Reduction of Tin Salts by Calcium.**—Only one compound, $CaSn_3$, has been shown to exist by the method of thermal analysis.[27] On adding stannous iodide to a calcium solution, a brownish precipitate is formed, while the solution becomes colorless. This precipitate is fairly reactive toward air and water.

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[26] Baar, *Z. anorg. Chem.*, **70,** 375 (1911).

[27] Tammaru, *ibid.*, **62,** 86 (1909).

The results of several determinations are given in Table X.

TABLE X

REDUCTION DATA, TIN

| Expt. | Ca | $SnI_2$ | Ca/Sn |
|---|---|---|---|
| 1[a] | 0.0547 | 0.0888 | 4.758 |
| 2[b] | .0444 | .0680 | 5.08 |

[a] Past end-point. [b] Very near end-point; solution slightly blue.

These experiments indicate that the ratio Ca/Sn has a value 5.0, corresponding to a compound of the formula $Ca_5Sn$. This compound does not occur in the literature.

**Reduction of Ethylmercuric Chloride by Sodium.**—Ethylmercuric chloride, like other organic metal halides, exhibits many of the properties of a salt in which the mercury-ethyl group acts as electropositive constituent. This group has, in fact, been obtained in the free state by cathodic precipitation in liquid ammonia solution.[28] It might be expected that, when ethylmercuric chloride is reduced by means of sodium, metathetic reaction would occur with the precipitation of the free group $C_2H_5Hg$. There are, however, two other possibilities: (1) a salt $NaHgC_2H_5$ of the group may be formed, as in the case of the corresponding trialkyl tin halides,[29] or (2) the bond between the ethyl group and mercury may be unstable in the presence of excess of sodium, in which case we should expect a hydrocarbon to be evolved and a sodium hydrargide of some kind to be formed.

While ethylmercuric chloride is moderately soluble in liquid ammonia, its rate of solution is very low, so that considerable time is required to complete a reaction when the salt is added to a solution of sodium. Reaction takes place more readily if the salt is first dissolved and sodium added to this solution; but the resulting product formed in this case is not necessarily identical with that formed in the first.

Ethylmercuric chloride was added to solutions of sodium in varying amounts and the point determined at which the blue color disappeared. The results are given in Table XI. The ratio Na/Hg, given in the last column, is based on the assumption that all the chlorine in the compound goes to form sodium chloride and that the balance of the sodium combines with mercury. There can be little doubt that for every equivalent of chlorine present in the compound one atom of sodium is used up to form sodium chloride; but it does not necessarily follow that all the remaining sodium is combined with mercury in the metallic precipitate formed, since it is conceivable that some other reaction may occur in which sodium is involved.

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[28] Kraus, THIS JOURNAL, **35**, 1732 (1913).

[29] Session, *Dissertation*, Clark University, **1924.**

TABLE XI

REDUCTION DATA, $C_2H_5HgCl_2$

| Expt. | Na | Salt | Na/Hg |
|---|---|---|---|
| 1[a] | 0.1305 | 0.4957 | 2.03 |
| 2[b] | .1305 | .5133 | 1.93 |
| 3[c] | .0952 | .3663 | 2.0 |
| 4[d] | .0952 | .3911 | 1.808 |
| 5[e] | .2786 | 1.1380 | 1.82 |
| 6[f] | .2980 | 1.1483 | 1.989 |

[a] Close to end-point; pale blue in main tube. [b] Color discharged. [c] Pale blue solution. [d] Color discharged. [e] Very pale blue solution. [f] Just transparent in main tube.

In several of these experiments, as may be seen from the table, the solution is very nearly colorless for the ratio Na/Hg = 2. If we bear in mind that the hydrargide initially precipitated tends to break up to form free sodium and a hydrargide richer in mercury, it is not surprising that in certain of these experiments the color was not completely discharged for values of the ratio Na/Hg $< 2$. If we assume that all the excess of sodium is present in the hydrargide and, further, that all the mercury is present in the same compound, we should be led to conclude that this compound has a composition corresponding to the formula $Na_2Hg$. We have already seen that in the reduction of ordinary mercuric salts the initial compound precipitated has a composition corresponding to the formula NaHg. In any case it may be concluded that the compound between the ethyl group and mercury is broken down and that all the mercury is present in the hydrargide. This was confirmed by washing the metallic precipitate repeatedly with liquid ammonia and then determining the mercury left behind in the precipitate. Several determinations yielded the following results: weight of ethylmercuric chloride, 1.1483–1.0646; weight of mercury in compound, 0.8703–0.8059; weight of mercury recovered, 0.8665–0.8029. All of the mercury of the compounds is therefore precipitated on treating with an excess of sodium. It was observed that during the course of the reaction a considerable quantity of permanent gas is evolved. This gas was collected and its vapor density determined. Two determinations yielded for the molecular weight the values 32.86 and 30.24, respectively. These agree closely with the molecular weight of ethane, 30.1. One might expect the process of reduction to take place as follows: $C_2H_5HgCl + 3Na = NaCl + Na_2Hg + {}^1/_2(C_2H_5)_2$. The molecular weight of the gas, however, indicates clearly that butane is not formed in the course of this reaction. In order to account for the evolution of ethane, it is necessary to assume that in some way ammonia is concerned in this reaction, supplying the hydrogen atom necessary to form ethane by combination with the ethyl groups of the compound.

Light is thrown on this reaction by the recent work of Sessions,[29] who has shown that when tetramethyl tin is treated with metallic sodium in liquid ammonia the following reaction occurs: $Sn(CH_3)_4 + 2Na + NH_3 = NaSn(CH_3)_3 + NaNH_2 + CH_4$. Sessions has interpreted this reaction as taking place in two stages, in the first of which two atoms of sodium react with one molecule of tetramethyl tin with the formation of the sodium trimethyl stannide and sodium methyl. Sodium methyl, then, hydrolyzes by interaction with ammonia, with the formation of sodium amide and methane. We may expect that, if the combination between the ethyl group and mercury is unstable in the presence of free sodium, a corresponding reaction will occur and that the reduction process of ethylmercuric chloride by means of sodium may be represented by the following equation: $C_2H_5HgCl + 3Na + NH_3 = NaCl + NaHg + C_2H_6 + NaNH_2$.

Because of the presence of the precipitated hydrargide in a finely divided condition, the concomitant precipitation of the amide, $NaNH_2$, would not be observable, and the ratio Na/Hg calculated for the reaction would have a value of 2, although the hydrargide actually has the composition NaHg. The evolution of ethane in the course of the reaction shows that hydrogen is involved and this can only be derived from the ammonia present, under which conditions the $NH_2$ group, which is comparatively stable, must almost inevitably form an amide by interaction with sodium. It may be mentioned that the hydrargide present in this reaction breaks down, on standing in the presence of ammonia, with the formation of a sodium solution and hydrargide which is necessarily richer in mercury than NaHg.

## Summary

The theory of the reduction of metals from their salts by means of more electropositive metals in liquid ammonia solution is developed and the various cases are discussed.

Data are given with respect to the reduction of salts of mercury, cadmium, zinc, tin, lead, antimony, bismuth, thallium and silver, by means of sodium. With the exception of silver, all the metals in this list form compounds with sodium. Certain of the intermediate compounds of sodium with mercury, tin and lead are not stable in the presence of liquid ammonia, breaking down with the formation of free sodium and compounds richer in the more electronegative element.

Data are also given in regard to the reduction of salts of silver, zinc, mercury, lead and tin by means of calcium. All these metals yield compounds with calcium.

The reduction of ethylmercuric chloride by means of metallic sodium in liquid ammonia solution has been studied. In the presence of an excess

of sodium, the compound NaHg which is formed appears to be identical with that formed in the reduction of ordinary salts of mercury under corresponding conditions.

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# THE DETERMINATION OF SURFACE TENSION FROM THE RISE IN CAPILLARY TUBES

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Richards, Speyers and Carver[1] in a recent paper describing a method of measuring surface tension by observations of capillary rise in two connected tubes refer to the equations of Rayleigh[2] for very narrow and very wide tubes and then state that "the problem presented by the intervening region has not as yet been solved mathematically." It is the object of this short paper to point out that a solution of this problem for all sizes of tube commonly used was given by the author three years ago.[3] Richards, Speyers and Carver refer to this paper as giving "a somewhat similar empirical method;" since however, it contains the corrections referred to below derived from a mathematical discussion of the equation to the meniscus and gives new absolute determinations of the surface tension of benzene and water at 20° it seems necessary to reaffirm the soundness of the theoretical methods employed by the author.

The chief feature of the 1921 paper is a new method of correcting the simple equation

$$\frac{2\gamma}{g(D-d)} = a^2 = rh \tag{1}$$

which is strictly true only for infinitely small tubes. Here $\gamma$ is the surface tension, $g$ the gravitational constant, $D$ the density of the liquid, $d$ the density of air + vapor, $r$ the radius of the capillary tube and $h$ the capillary rise measured from a plane surface of the liquid. Of the numerous formulas which have been devised to correct this equation for larger values of $r$, the most precise is that of Rayleigh[2] which may be put in the form

$$a^2 = rh\left(1 + \frac{1}{3}r/h - 0.1288\frac{r^2}{h^2} + 0.1312\frac{r^3}{h^3}\right) \tag{2}$$

Inspection of this formula shows from its mathematical form that it can only be used for a limited range and it is pointed out below that when $r/h$ is greater than 0.4 the error introduced by the use of this formula in-

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[1] Richards, Speyers and Carver, THIS JOURNAL, **46**, 1196 (1924).

[2] Rayleigh, *Proc. Roy. Soc.*, **92A**, 184 (1915).

[3] Sugden, *J. Chem. Soc.*, **119**, 1483 (1921).