SOME RECENT CONTRIBUTIONS TO OUR KNOWLEDGE OF METALLIC REDUCING AGENTS.[1]

BY H. F. KELLER.

IN the extraction of metals from their oxygen compounds, carbon is certainly the most important and useful reducing agent. Its great affinity for oxygen is utilized in the manufacture of iron and steel; the commercial production of other useful metals, such as copper, lead, zinc, and tin is accomplished, either directly or indirectly, with its aid; and under its influence even the energetic metals of the alkalies release their powerful grip upon oxygen. Contrasted with this, the use of other substances for the purpose of abstracting oxygen is almost insignificant. Is it surprising, therefore, that carbon is looked upon as the reducing agent *par excellence*, or that the very idea of reduction seems to us inseparably associated with this element?

But the reducing power of a substance depends, in a large measure, upon temperature. It is well known to chemists that, under certain conditions, many metals have affinities which are far more powerful than those of carbon. When we glance over the pages of our chemical text-books, we see described there numerous experiments based upon the superior combining power of iron, aluminum, zinc, magnesium, and the alkali metals. The great Swedish chemist who arranged the elements according to their supposed affinities in an electro-chemical series, was among the first to employ the positive alkali metals for isolating and preparing other elements. His method consisted in decomposing the halogen compounds by means of potassium; and it was subsequently improved by Berzelius' distinguished disciple, Wöhler. With its aid, the latter chemist not only succeeded in reducing for the first time those remarkable metals, aluminum and glucinum, but he also showed that *all* those metals, the oxides of which cannot be reduced by either carbon or hydrogen, may be obtained by the action of potassium upon their halogen compounds.

It must not be supposed, however, that the use of metals as reducing agents is confined to the laboratory and the lecture

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table. Practical applications of such reactions may be less conspicuous, but they constitute, nevertheless, the basis of not a few important metallurgical processes. The "precipitation" of lead from its sulphide ores; the solution of silver by the nascent lead in the blast-furnace; the amalgamation of the same metal in the iron pan; Deville's process of extracting "silver out of clay," recently so greatly perfected by Castner and Netto—are they not essentially reductions by means of metals?

In view of the facts mentioned, it may appear strange that comparatively little progress was made for many years in the study of the reducing properties of metals. We can, however, satisfactorily account for this when we consider the great tendency of metals to form alloys; it is difficult, in many cases indeed impossible, to obtain products entirely free from the reducing metal, and it is also well known that even a trifling amount of such an impurity may seriously impair the valuable qualities of a metal. Another obstacle has been the high price of those metals, which, by reason of their more powerful affinities, could, with advantage, be substituted for carbon.

Recent improvements in the commercial production of some of these metals have partially removed the latter obstacle. Thanks to the rapid progress of electro-metallurgy, aluminum is now to be had for about half a dollar per pound; sodium, once a chemical curiosity, is manufactured on an enormous scale at a less cost even than aluminum; and magnesium, now successfully extracted from carnallite, is applied to a variety of technical uses.

The radical changes which have taken place in our views on chemical affinity, as a result of the study of thermo-chemical phenomena, and the theory that the properties of the elements are *periodic functions* of their atomic weights, have also largely contributed to awaken interest and activity in the subject of our discussion.

The remarkably high heats of formation of its oxide and chloride, as well as the great stability of these compounds, render the action of magnesium upon other oxides and chlorides particularly interesting. Clemens Winkler, of Freiberg, has presented us with a most careful and systematic investigation of the reducing action of this metal upon oxides, while Seubert and Schmidt have communicated a similar exhaustive study of its action upon chlorides.

In giving a brief résumé of the results obtained by these experimenters, I shall adhere to the order adopted by them. It is based upon the periodic system, and has the advantage of showing many interesting relations that might otherwise escape notice.

GROUP I.

Group I embraces a main group consisting of lithium, sodium, potassium, rubidium, and cesium, and a sub-group consisting of copper, silver, and gold.

Owing to the difficulty of obtaining the oxides of the alkali metals in a pure condition, the carbonates were employed. It was found that to insure the best results three atoms of magnesium are required for every molecule of the carbonate, thus: $Na_2CO_3 + 3Mg = 3MgO + C + 2Na$.

The carbon as well as the sodium are deprived of their oxygen. It was found that, with the exception of cesium carbonate, the alkaline carbonates *suffer reduction* to the metallic state when heated with magnesium, but that the intensity of the reaction diminishes as the atomic weight of the metal increases. Lithium, *e. g.*, whose atomic weight is only seven, was reduced with explosive violence, the metal being completely vaporized, while the tube in which the reduction was effected was shattered to pieces; potassium (atomic weight 39), and rubidium (atomic weight 85) on the other hand, were reduced quickly and without notable vaporization.

The reduction may be made in a tube of hard glass closed at one end; it is better observed, however, by conducting it in a current of hydrogen.

The preparation of potassium affords a most instructive experiment, which may well serve for lecture demonstration.

Into a wide tube of Bohemian glass, a porcelain boat, containing about two grams of the mixture of potassium carbonate, and magnesium is introduced. A current of perfectly dry hydrogen gas is passed through the tube, and the part of the tube surrounding the boat is gradually heated to incipient redness;

the mass darkens, and upon further raising the temperature with the aid of the blast-lamp, the reduced potassium is completely expelled from the boat, exhibiting the deep green color of its vapor, and is deposited in the form of a bright mirror in the cooler part of the tube. At the same time the hydrogen flame shows an intense violet color. The dark residue remaining in the boat consists of magnesia and carbon. Enough potassium will have collected to show its color, luster; that it is sectile, fusible; its action upon water, bromine, etc.

In view of the high price of metallic potassium, the question as to whether the described reaction might not be carried out on the large scale suggested itself. Experiments showed, however, that in the absence of a gas current, the distillation of the metal is very incomplete; and inasmuch as carbon monoxide forms an explosive compound with this metal, illuminating gas could not be substituted; in fact, the explosive carbonyl-potassium was invariably formed when the quantity of magnesium present was insufficient for the *complete* reduction of the carbonate.

This was further proved by experiment. When two atoms only of magnesium were taken, the reaction took place according to the equation:

$$CO\genfrac{}{}{0pt}{}{OK}{OK} + 2Mg = CO + 2K + 2MgO.$$

More promising results were obtained by employing potassium hydroxide instead of potassium carbonate. The danger of forming the explosive body is thus avoided, while the hydrogen gas set free simultaneously with the potassium, insures the complete distillation of the latter:

$$KOH + Mg = K + H + MgO.$$

The reaction is somewhat violent, but may be moderated by adding some inert substance, such as magnesia, or by using the magnesium in the form of lumps or bars.

Winkler says "it does not seem unlikely that the manufacture of potassium could be carried out by means of the same apparatus, and the same operations, which C. Netto has so successfully employed in reducing caustic soda with carbon. Into a retort filled with bars of magnesium, and heated to redness, melted potash would be allowed to flow in a continuous stream, while the escaping mixture of potassium vapor and hydrogen is being cooled."

Winkler figures the cost of a pound of potassium to be about $3.75; the metal is now quoted at $28.

Beketow, who had previously made use of the action of aluminum upon potassium hydroxide, obtained only one-half of the theoretical yield owing to the simultaneous formation of potassium aluminate.

The sub-group, consisting of the heavy metals copper, silver, and gold, exhibited the reverse behavior; the reduction was more energetic the higher the atomic weight of the metal. A very *slight* deflagration accompanied the removal of oxygen from cuprous oxide, while silver oxide was reduced with *explosive violence*. Very curiously aurous oxide was not visibly affected by the magnesium. This is explained, however, by the fact that gold oxide splits up into its constituents considerably below the ignition point of magnesium.

GROUP II.

The main group comprises glucinum, magnesium, calcium, strontium. and barium; and zinc, cadmium, and mercury, constitute the sub-group.

These elements are bivalent, and the action of their oxides upon magnesium is therefore:

$$R''O + Mg = MgO + R''$$

In some cases the *hydroxides* were also used.

Glucina was easily reduced by magnesium; the mass became slightly incandescent, but some unaltered oxide was found in the residue.

There was no action observed when a mixture of magnesium and magnesia was heated in hydrogen; the oxide remained in the boat, while the metal sublimed in beautiful crystals. The existence of Beetz's suboxide could not be confirmed.

No visible sign of chemical action occurred when lime and magnesium were heated together. The reduction proved nevertheless to be almost complete.

A slight incandescence attended the reduction of strontia, whilst barium oxide displayed an energetic action upon magnesium. In both cases the decomposition was apparently complete.

None of the alkaline earth metals were found to be volatile at the temperature of reduction.

The hydroxides were even more readily acted upon than the oxides; so striking and beautiful, indeed, were the phenomena observed in the cases of calcium hydroxide and strontium hydroxide, that Winkler proposes to utilize them for lecture illustration, and in pyrotechnics.

The reduction of the oxides belonging to the sub-group was very energetic, the resulting metals being vaporized completely. Cadmium oxide develops less energy than either zinc oxide or magnesium oxide.

Both in the main group and the sub-group, the maximum of chemical energy occurs in the second member.

GROUP III.

The main group embraces boron, aluminum, (scandium,) yttrium, lanthanum, and ytterbium, and gallium, indium, and thallium, form the sub-group. Three atoms of magnesium are required to abstract the oxygen from their oxides:

$$R_2O_3 + 3Mg = 3MgO + 2K'''$$

Phipson has observed that boric acid is reduced upon ignition with magnesium. With the aid of magnesium, boron was also obtained by Geuther from the boro-sodium fluoride, and quite recently L. Gattermann has shown that boric acid, as well as borax can be reduced by means of this metal, so as to yield products which are suitable for the preparation of various volatile boron compounds.

Winkler confirmed these observations. He states that the trioxide and the borate of sodium are easily reduced, the latter with much energy and evolution of sodium vapor. But he found that, instead of free boron, the residue contains magnesium boride of variable composition; for, on treatment with hydrochloric acid, boron hydride is given off as a gas. Sometimes a solid residue remains, which is likewise a compound of boron and hydrogen.

Owing to the acid-forming character of boron, the reduction was never complete; borates, upon which magnesium has no action, are always formed.

An attempt was also made to prepare a boron suboxide by. limiting the supply of magnesium, thus:

$$B_2O_3 + Mg = 2BO + MgO$$

but no indication of such an oxide was observed.

A dark colored product resulted from heating alumina with magnesium. The reaction appeared to be quite energetic; the mass exhibited a vivid glow and increased largely in volume. In addition to finely divided aluminum, a new oxide, AlO,. and magnesium spinel had been formed. This monoxide could not be obtained in a pure condition, but its existence was proved beyond doubt. It is best prepared by heating in a current of hydrogen, a mixture corresponding to

$$Al_2O_3 + Mg = 2AlO + MgO.$$

This oxide is a brownish-black, voluminous powder, is pyrophoric, and liberates hydrogen slowly from water; it precipitates cuprous oxide from copper sulphate solution, and is exceedingly susceptible to oxidation.

Winkler suggests that the blue color of sapphire, and possibly also that of ultramarine, may be due to a small proportion of this monoxide.

Of the rare earths of group III, only yttria and lanthana were subjected to the action of magnesium. The energy of the reduction appeared to increase with the atomic weights.

Upon the oxides of the sub-group, magnesium reacts with great violence; the intensity of reduction has its maximum in In_2O_3.

The behavior of Tl_2O_3 towards magnesium, appears to be an exception. Before the temperature of reduction is reached, this oxide splits up into Tl_2O and O_2, and the thallous oxide so formed is then only partially reduced. Thallium carbonate, however, is deprived of its oxygen completely and with explosive violence.

GROUP IV.

The most interesting results, perhaps, were obtained in the fourth natural group of elements.

The known properties of carbon, silicon, titanium, zirconium, cerium, and thorium, assign them positions in the main group, while germanium, tin, and lead, constitute the sub-group.

In addition to their acid-forming dioxides, the majority of these elements are capable of giving monoxides. It was therefore deemed desirable to attempt not only the complete reduction of the higher oxides, but also a *partial* removal of the oxygen with a view to procure the lower oxides.

The statements of different experimenters concerning the action of carbon dioxide upon magnesium are somewhat conflicting.

That a ribbon of the metal will burn in an atmosphere of carbon dioxide was first observed by Kessler, but neither he nor other chemists who repeated and modified his experiment explained satisfactorily the nature of the reaction.

Winkler shows, in the first place, that magnesium, when *moderately* heated in a current of carbon dioxide, does not take fire, but is slowly converted at its surface into a carbide, carbon monoxide being formed at the same time. Upon increasing the heat to a full redness, the metal was inflamed and continued to burn with a dazzling light. The products of this combustion are magnesia and carbon.

When the magnesium is employed in the form of powder, these reactions take place even more readily. At a temperature considerably below a red heat carbon monoxide appears, and its quantity is greatly increased when low redness is reached. The metal burns with great brilliancy at a full red heat, and unless the current of carbon dioxide is very rapid, its reduction is complete.

It has already been mentioned that a separation of carbon was observed when magnesium acted upon carbonates: also that carbon monoxide was formed when an excess of the carbonate was present. Further experiments were made with calcium carbonate. A mixture of this substance with magnesium: $CaCO_3 + 3Mg = Ca + C + 3MgO$, heated in a current of hydrogen detonated violently. The examination of the débris, revealed the presence of a carbide of magnesium. No metallic calcium was observed in the residue when only two atoms of magnesium were used for each molecule of the carbonate.

According to Kessler, burning magnesium is extinguished in carbon monoxide, while Parkinson asserts that at a red heat the metal burns vividly in this gas. Both observations were found to be correct. A spiral of magnesium wire ignited in the air, ceased to burn while introduced into a jar of carbon monoxide, but when strongly heated in a current of the gas the magnesium emitted light, and a gray coating of a carbide appeared on its surface.

Numerous experiments to determine the exact composition of this carbide were made, but without yielding a definite result.

Silicon exhibits a pronounced tendency to combine with magnesium. Silicon-magnesium was first observed by Wöhler, in 1858.

The reduction of silica by metallic magnesium was observed in 1864, by Phipson, and Parkinson showed in 1867 that silicon-magnesium, as well as a magnesium silicate, are formed at the same time. A few years ago L. Gattermann published an interesting paper, in which he showed how very easily silicon dioxide is reduced by magnesium. He states that either silicon or silicon-magnesium can be obtained by varying the proportion of magnesium; and he applies the reaction to the preparation of volatile compounds of silicon, such as the chloride, bromide, iodide, silicoformic acid, silico-chloroform, etc.

Gattermann and Winkler agree that an energetic reaction occurs upon heating a mixture of one molecule of silica and two atoms of magnesium.

$$SiO_2 + 2Mg = Si + 2MgO.$$

By adding magnesia to the mixture, the heat of the reaction was moderated, but it was then found that much silicon-magnesium was contained in the product. If the reaction be effected at low temperature and in the presence of an excess of magnesium, silicon-magnesium is always formed, while at a high heat or in presence of magnesium, only amorphous silicon results.

A silicon monoxide could not be obtained by the reduction of silica, either by magnesium or silicon.

Many silicates are reduced quite as easily as the dioxide; in some cases the metallic base is likewise reduced, *e. g.*, potash glass.

None of the oxides studied presented greater difficulties than titanium dioxide. The results may thus be summed up: Titanium dioxide was not reduced to the metallic state; a mixture of monoxide and a titanium spinel were the products of the reaction. Other intermediate oxides were sometimes formed. When the residue was treated with hydrochloric acid, HTi_3O_4 was formed, which, upon heating, gave TiO_2 and hydrogen. Neither titanium-magnesium, nor a titanium hydride, was observed.

The reduction of zirconia was effected by heating it with magnesium to a high temperature. A monoxide could not be identified with certainty; and $ZrMg_2$ does not appear capable of existing.

According to the amount of magnesium employed either cerium or Ce_2O_3 were obtained from cerium dioxide. An intermediate monoxide was not formed. The reduction begins at a moderate red heat and is accompanied by a vivid glow. A considerable proportion of the magnesium is volatilized. In the nascent state, cerium was found to absorb hydrogen in large quantities.

The formation of a metallic hydride at a bright red heat is a most remarkable observation. It is clearly proved to be correct by the following experiment.

A mixture is prepared according to the equation:

$$CeO_2 + 2Mg = Ce + 2MgO$$

Twenty grams of this mixture are placed in a combustion tube through which a current of dry hydrogen is passed, while a gentle heat is applied to expel any moisture. The further end of the tube is then closed with a strong clip. Hydrogen is allowed to enter the other end and the heat quickly raised to bright redness; a rapid current of hydrogen is seen to pass through the wash-bottles into the tube.

The hydride is of a brownish-red color. It is without action on water at ordinary temperatures, but sets free hydrogen upon heating. Hydrochloric acid dissolves it to $CeCl_3$, with evolution of hydrogen. It was found impossible to completely remove magnesia from the product. The hydride is very inflammable, and detonates with potassium chlorate, potassium nitrate, etc.

The analytical results obtained point to the formula CeH_2.

After the existence of a cerium hydride had thus been established, the thought suggested itself that the other elements of Group IV might possibly be capable of forming similar compounds. Only carbon and silicon were known to form hydrides, but these elements could not be made to unite with hydrogen when their oxides were reduced by magnesium. Since titanium could not be reduced to the metal, it is not strange that all efforts to form a hydride gave negative results; zirconium and thorium did absorb hydrogen and yielded hydrides similar to CeH_2. The same was observed with lanthanum and this led Winkler to believe that this element belongs to the cerium group; but he showed subsequently that yttrium and other trivalent elements, and even the divalent barium, strontium, and calcium can unite with hydrogen.

These hydrides represent a new class of metallic compounds, in which only half the usual valence of the metals is satisfied.

The action of magnesium upon chlorides has been made the subject of an elaborate research by Seubert and Schmidt.

I must content myself with a very brief statement of some of the main results obtained by these chemists.

Both the anhydrous bodies and the aqueous solutions of the chlorides were subjected to the action of magnesium.

In the former case the substance, either mixed with magnesium powder, or conducted over it in the form of vapor, was heated to a high temperature. It was found that all chlorides could thus be reduced to the metallic state, but the reduction was incomplete in the groups of the metals of the alkalies and the metals of the alkaline earths.

In *neutral* aqueous solutions, all the metallic chlorides, save those of the alkalies and those of the alkaline earths, gave up their chlorine to the magnesium. In some cases the metals were deposited in the metallic state, (silver, gold, thallium, lead, arsenic, antimony), but in most cases, hydroxides were precipitated. These hydroxides always represent the lowest state of oxidation. $CuCl_2$, *e.g.*, is changed into Cu_2O; chromium, aluminum, iron, manganese, cobalt and nickel, all yielded hydroxides.

It would seem that the tendency to form such hydroxides is peculiar to the positive metals, and especially to those forming basic salts. Seubert and Schmidt believed this to be due to a dissociation of the chlorides into hydroxides and hydrochloric acid. They suppose, for instance, that an aqueous solution of $AlCl_3$, contains $Al(OH)_3$, $3HCl$. This view is rendered quite probable by the fact that solutions of copper, nickel, cobalt, and chromium exhibit the color of their *hydrated* salts.

Of other metals whose oxides possess a high heat of formation, aluminum has found some application in the reduction of oxides. Beketow has employed it with success to prepare some of the metals of the alkalies; and the experiments of Greene and Wahl of reducing manganese oxides by means of metallic aluminum are still fresh in our memory.

I am convinced that a continued study of the relative affinities of the metals for oxygen and other negative elements, will lead to important applications in metallurgy, and give new and valuable methods to synthetic and analytical chemistry.

OBSERVATIONS ON AMERICAN OIL OF TURPENTINE.

BY J. H. LONG.

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IN the February, 1893, number of the *Journal of Analytical and Applied Chemistry* I called attention to certain peculiarities of our American turpentine-oil as distilled from the crude turpentine produced in the southern states.

It is well known that the chief difference between the so-called French and American turpentines is found in their behavior toward polarized light, the French oil being laevo-rotatory, while that produced here has always been described as dextro-rotatory.

In the course of the examination of a large number of samples distilled in the laboratory from fresh crude turpentine sent me directly, I found that some disclosed a very low rotation, and a few were even laevo-rotatory. Through the courtesy of Mr. E. B. Martin, of Louisville, I was supplied with crude "gum" collected in small amounts from single trees, and from the tests of these samples it appeared that the laevo-rotation was