

cock, and from the fact that blasting invariably reduced the weights, it seems probable that, in the case of some of the elements, at least, an oxide of a higher state of oxidation was more stable over the Bunsen burner than over the blast-lamp. Such behaviors have been noticed with some of the more common elements.

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FLUORIDE OF GOLD.¹

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INASMUCH as fluorspar is frequently associated with gold in nature, and quite notably so in the deposits of the telluride ores, it has seemed important to study gold fluoride in order to determine, if possible, whether this substance can play any part in the genesis of these deposits.

The known compounds of gold with the halogens chlorine, bromine and iodine, are, as a rule, fairly well defined. In the trivalent condition, gold forms the relatively stable chloride while the bromide and iodide show greater tendency to break down into the lower state of valence of gold.

The halides in which gold shows a monovalence have received considerable attention, and it is known with a reasonable degree of certainty under what conditions aurous chloride, bromide, and iodide are capable of existence.

While the chlorides, bromides and iodides of gold have received more or less study, comparatively little is known of fluoride of gold. Prat² has prepared an intermediate oxide of gold, Au_2O_2 , by the incomplete solution of gold in aqua regia, in which the hydrochloric acid is in excess, treating the solution with sufficient potassium bicarbonate to dissolve the precipitate formed, and warming the clear orange-yellow solution to 95° , when a dark olive-green precipitate was obtained which, when dried, showed the composition Au_2O_2 . In studying the properties of this oxide, Prat states that hydrofluoric acid combines with it but without dissolving it. In his study of the action of fluorine on the various metals, Moissan states that at a red heat, gold is attacked by

¹ Read before the Wisconsin Academy of Science, December 26, 1902, and published in the *Transactions*.

² *Compt. rend.*, **70**, 843.

fluorine gas, a yellow hygroscopic substance being formed, and that this substance is readily decomposed into gold and fluorine.

These two experiments give practically what is known of the fluoride of gold.

The activity of the halogens toward other elements is, as a rule, inversely proportional to their atomic weights. The first member of this group of active elements, fluorine, is certainly the most active of all the elements, be they halogens or not; yet, as will be demonstrated later, it appears to have little if any affinity for gold.

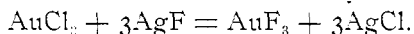
In studying the chemistry of gold, it should always be borne in mind that it is the most inactive of the metals, but the relative stability of the most of its salts, notably with the halogens, would appear to make probable the relative stability of the compound of the most active of the elements, fluorine. On the other hand, we have the marked difference of fluorine from the other halogens in the insoluble fluorides of calcium, strontium and barium, as contrasted with the very soluble chlorides, bromides and iodides; and the soluble fluorides of silver and thallium as compared with the insoluble chlorides, bromides and iodides.

In order to study the relations between fluorine and gold, experiments were conducted with the view of bringing about, if possible, the formation of gold fluoride under various possible conditions.

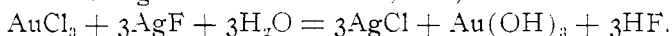
The first experiment made was a study of the action of hydrofluoric acid on gold oxide. To this end, gold oxide was prepared by the action of magnesium oxide on a solution of gold chloride and the excess of magnesia removed with nitric acid. The gold oxide thus obtained was finely divided, and hence in the most suitable condition to be susceptible to any chemical action. This gold oxide can remain in contact with hydrofluoric acid indefinitely or, as has been the case, can be boiled for weeks with either hydrofluoric acid alone or with a mixture of hydrofluoric and nitric acids, without suffering any change whatever. These experiments have been repeated several times, but in no case has gold been found to enter into solution, nor has it been possible to detect fluorine in the precipitate. It is obvious that gold fluoride cannot be prepared by the action of hydrofluoric acid on the oxide. The next most natural method to try

for the preparation of the fluoride would be that of double decomposition.

Silver fluoride and gold chloride, both being soluble salts, on being brought in contact in solution should yield theoretically:



The actual case is that when solutions of these two salts are brought in contact, gold hydroxide is quantitatively thrown out of solution along with silver chloride; thus,



The accuracy of this reaction has been carefully established in the laboratory.

If gold fluoride is even momentarily formed, it is immediately decomposed by water.

The method yet remaining for the preparation of a substance incapable of existence in presence of water would be the use of anhydrous solvents. A large number of organic solvents have been tried with this end in view, but no substance has been found which would dissolve both gold chloride and silver fluoride; either these salts are insoluble or are decomposed by the substances worked with. Among the solvents examined, mention may be made of the following: Alcohol, ether, carbon bisulphide, benzene, turpentine, pentane, hexane, chloroform, carbon tetrachloride, ethyl nitrate, nitrobenzene, ethyl acetate, ethyl propionate, and pyridine.

It thus appears that gold fluoride is incapable of existence not only in presence of water, but under the ordinary conditions met with in the laboratory and in nature.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI, No. 60.]

A METHOD FOR THE ESTIMATION OF CHLORIDES, BROMIDES AND IODIDES.

BY STANLEY BENEDICT AND J. F. SNELL.

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IN THE August number of this Journal we described a method for the detection of chlorides, bromides and iodides in presence of each other. The reagent used to liberate the iodine and bromine was potassium iodate, which sets free the iodine on acidifi-