SOLUBILITY OF GOLD IN CERTAIN OXIDIZING AGENTS.[1]

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THE inactive character of gold is so pronounced that towards many of the reagents the element is quite indifferent, in fact, almost the only solvents in general use for dissolving the metal are chlorine, bromine, or a solution of alkaline cyanide in presence of atmospheric oxygen. Chlorine and bromine attack the metal readily, while iodine only dissolves the metal when it is freshly liberated, or under other very favorable circumstances. The metallic perchlorides, perbromides and periodides, according to Nicklès,[2] dissolve gold, the lower halides of the metal being formed along with gold chloride. Hot selenic acid readily dissolves gold. Iodic acid has slight action on the metal, while, according to Prat,[3] a mixture of iodic and sulphuric acids dissolves gold when heated to 300°. This reaction has been verified by the author, who also finds that gold is readily soluble in a mixture of hot sulphuric and periodic acids.

Gold is also slightly soluble in the alkaline sulphides and thiosulphates.[4]

There is another class of substances, substances which evolve oxygen when treated with acids, whose action on gold has received very little attention.

Several years ago the author had occasion to review the work of Mitscherlich on the solubility of gold in selenic acid, and showed that gold is readily attacked by pure hot selenic acid with the formation of auric selenate.

In following the same line of work with telluric acid, which in many respects is closely analogous to selenic acid, the obstacle is met that telluric acid is a solid. This apparent difficulty can be obviated by first dissolving the crystalline telluric acid in sulphuric or phosphoric acid. Such a solution of telluric acid, when heated, dissolves metallic gold.

With the fact at hand that at the same temperature at which selenic acid or a solution of telluric acid attacks gold, the acids themselves are broken down into the dioxides and oxygen it ap-

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[1] Read at the St. Louis meeting of the American Chemical Society.

[2] *Ann. Chim. Phys.* (4), X, 318.

[3] *Compt. rend.*, **70**, 840.

[4] Stedefelt: "Lixiviation of Silver Ores," pp. 15, 38.

peared probable that the solvent action in these cases was due to the production of oxygen in the reaction. Should this view be correct, gold should be soluble in acids when an oxidizing agent is present. The action of a large number of substances, such as oxides of various types, sulphates, etc., was tried on gold in presence of sulphuric, phosphoric and arsenic acids, and only such substances as give oxygen in presence of the acids will act on gold. In most cases, the only precautions necessary in order to demonstrate the solvent action is to have the acids in a high degree of concentration.

All of the substances that have been used in the following experiments were carefully tested for the halogens and only such substances used as were halogen-free. In many instances the substances had to be prepared in order to obtain them in a high degree of purity. The author wishes to acknowledge the services of Mr. Geo. Kemmerer, who greatly assisted the work at many points, both in preparing many of the substances used and in confirming the reactions.

The first substance that was naturally examined was manganese dioxide, as it is well known that manganese dioxide gives oxygen when heated with sulphuric acid. A mixture of manganese dioxide and sulphuric acid, when heated for a few minutes with gold, causes the metal to go into solution. On diluting the solution and testing with oxalic acid or ferrous sulphate, all of the gold is precipitated. In working with manganese dioxide and sulphuric acid, practically the only precaution necessary is to have the acid concentrated. Solution of gold in presence of manganese dioxide and sulphuric acid takes place readily when the mixture is hot, but the reaction also takes place in the cold. A mixture of manganese dioxide and sulphuric acid, when allowed to remain in contact with gold leaf for twelve hours at 0°, will dissolve sufficient gold to give an appreciable precipitation, when the mixture is diluted and treated with ferrous sulphate. It is thus seen that while heat accelerates the reaction, solution nevertheless takes place at low temperatures.

The higher oxides of manganese act in an entirely similar manner. The substances actually worked with were manganese dioxide (*a*) native, (*b*) from the ignition of manganese nitrate, (*c*) by the action of bromine on manganese acetate: Manganese sesquioxide (Mn_2O_3), manganese protosesquioxide (Mn_3O_4), and potassium permanganate. The solvent action takes place in a similar manner when phosphoric or arsenic acid is substituted for sulphuric, but the action is greatly moderated.

In 1872 Allen[1] showed that when solid potassium permanganate and sulphuric acid are heated for a few minutes with precipitated gold the solution becomes nearly clear, and on diluting and testing with oxalic acid or ferrous sulphate the solution was found to contain abundance of gold.

This experiment has been repeated, using sulphuric acid as described by Allen, and also by substituting phosphoric for the sulphuric acid. In all cases solution takes place and the gold can be readily detected by ferrous sulphate.

Lead dioxide, lead sesquioxide and red lead, when used with sulphuric acid, cause gold to enter into solution. The action takes place more readily in the warm than in the cold, though at the ordinary temperatures solution does actually take place, gold being found in the solution after several hours' contact.

With the higher oxides of lead, phosphoric acid can be substituted for the sulphuric acid, solution being affected. With chromium trioxide, chromium tetroxide and nickelic oxide, solution of gold is effected in presence of sulphuric or phosphoric acids, the reaction taking place, though moderated, in the cold.

When nitric acid is subjected to heat, more or less decomposition is effected, part of the acid breaking down into nitrogen dioxide and oxygen. This reaction can be used in a highly satisfactory manner to demonstrate the solubility of gold in sulphuric acid in presence of an oxidizing agent. This reaction was first noted by Reynolds,[2] and later by Spiller.[3] The results which these chemists obtained have been confirmed by the author and show that when a mixture of hot nitric and sulphuric acids comes in contact with gold the metal enters into solution and, at the same time, a lower oxide of nitrogen is formed by the reduction of the nitric acid and this oxide remains in the solution.

That a lower oxide of nitrogen is present in the solution after the gold has dissolved can be demonstrated in a very pretty manner, as Spiller has shown, by adding the solution to water when

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[1] *Chem. News*, **25**, 85.

[2] *Ibid.*, **10**, 48, 167, 277.

[3] *Ibid.*, **10**, 173.

the metal is thrown out as a purple precipitate. Allen[1] later showed that this precipitation by water from nitric-sulphuric acid solution is due to the presence of a lower oxide of nitrogen, probably nitrous acid, since when the water used for dilution contains potassium permanganate no precipitation takes place. Also ammonium sulphate destroys the nitrous acid and, after boiling with ammonium sulphate, no precipitation takes place, while when fuming nitric acid is added to any of the liquids, the gold is thrown down, purple in color. While Reynolds, Spiller, and Allen have studied the reaction of a mixture of hot nitric and sulphuric acids on gold, the influence of temperature on the reactions seems to have escaped their attention, and also that certain other acids as phosphoric acid can be substituted for the sulphuric acid with practically as great solvent action taking place.

While a mixture of nitric acid with either sulphuric acid or phosphoric acid readily acts on gold when warm, solution actually takes place, though more slowly, even at zero.

The action of oxygen gas on gold leaf, suspended in hot sulphuric acid, was also tried, but neither oxygen nor ozone would ause any of the metal to pass into solution.

The anode oxygen, obtained in electrolysis, was next studied s to its action on gold. Bunsen noticed, when using for the lectro decomposition of water an apparatus in which the platinum lectrodes were connected with the terminals by means of gold older, that on electrolyzing in presence of dilute sulphuric acid here is a film of oxide formed on the gold. Later it was shown y Spiller that when a plate of metallic gold is made the anode nd a piece of platinum foil or gauze used as the cathode in an lectrolyte of sulphuric acid or a mixture of nitric and sulphuric cids, the gold anode dissolves and the metal was deposited on e cathode, the source of the current used being a few Grove lls.

This work, which has been repeatedly verified, demonstrates at in presence of strong sulphuric acid, solution of gold can be fected readily by means of anode oxygen, the action proceeding pidly when the acid is hot. On the other hand, when the acid dilute the oxide of gold formed does not pass through the solun and deposit on the cathode as metal, but remains as an incrusta-

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[1] *Chem. News*, **25**, 85.

tion on the gold anode. Here again a similar series of results is obtained when phosphoric acid replaces the sulphuric. When solutions of the acid sulphates of potassium or sodium are used as electrolytes, the action goes on exactly as above indicated. If the solution contains sufficient free acid, gold passes through the electrolyte, while if the solution is dilute or contains only a little free acid, the oxide remains as a film on the anode.

In the case of an alkaline electrolyte, such as a solution of sodium or potassium hydroxide, it is possible for some of the gold to pass through the solution, probably from the formation of aurate of the alkali. Such is actually the case, although in alkaline solution a large amount of oxide remains as an incrustation on the gold anode employed. When neutral salt solutions are employed as electrolytes, such as the nitrates or sulphates of potassium or sodium, very little, if any, of the gold can pass through the electrolyte, and as a result the anode is converted into the oxide Au_2O_3. Here we have the last step in the series of experiments, *viz.*, obtaining the gold oxide in pure condition and retaining it as such.

In the above series of experiments the current used was 0.3-0.5 ampere at a pressure of 5 volts, the anode being a sheet of gold and the cathode a 20-gram platinum crucible. In such experiments where gold was deposited on the crucible, the quickest method found for removing the metallic deposit, which frequently appeared as a hard plating, was found to be the hot mixture of nitric and sulphuric acids, as indicated above. This method was found to be vastly superior to that of the use of a cyanide solution, such as was at first used.

It thus appears that gold is not only attacked by the halogens, but is also readily attacked in a large number of reactions in which oxygen is produced, these latter reactions taking place readily in the warm solutions, but slowly even at as low a temperature as zero. Furthermore, it appears that it is necessary for the oxygen to be produced in the mixture and that ordinary oxygen gas, when conducted into sulphuric acid in which gold leaf is suspended, will not cause the gold to dissolve.

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