SILVER AS A REDUCING AGENT.

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As has been pointed out, silver, in a finely divided condition, is dissolved by ammonia in the presence of atmospheric oxygen, and it slowly reduces a neutral solution of potassium permanganate.[1]

It occurred to the writer that it might be of interest to study in a systematic and quantitative way the behavior of finely divided silver toward substances that readily give up oxygen, such as chromic, chloric, bromic, iodic and permanganic acids. Thus far the action of silver on chromic, chloric and iodic acids has been studied and the results and related problems are of sufficient interest to make the author desirous of studying the subject somewhat exhaustively. It is deemed best, in view of the absence of aid and the small amount of time at his disposal, to give some of the results in this preliminary statement and reserve the details for a future communication.

Three separate preparations of silver were made, two from the ordinary commercial nitrate, and one, which was used in most of the following experiments, from pure silver obtained by the method of Stas. In each case the silver was precipitated from an alkaline solution of silver oxide by formaline. It was washed and heated alternately with ammonia and dilute sulphuric acid, and washed until every trace of the acid was removed. The preparations were dried and heated at various temperatures, from 125°, in one case, to low red heat in another.

Action of Silver on Chromic Acid.—A solution of potassium bichromate was prepared by weighing the salt which had been obtained by crystallizing three times from water the chemically pure salt of commerce, and drying to constant weight. The salt was heated for two hours in a porcelain crucible in an air-bath at 120°, and then during two-hour periods at 150°, 170°, 200° and 300°. The crucible was then placed upon a triangle in a large porcelain crucible which served as an air-bath and which was heated with the full burner flame for two hours, when the salt showed incipient fusion. Its weight remained perfectly constant above 200°, and 17 grams lost only a few milligrams above 120°. From this salt

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[1] M Carey Lea: *Ztschr. anorg. Chem.*, **3**, 180.

and water obtained by fractionally distilling ordinary distilled water, a fifth-normal solution with respect to its oxidizing power was made, containing 9.8166 grams to 1 liter.

Weighed amounts of silver, about 1 gram in each case, were heated, sometimes in a covered beaker and sometimes in a flask with an air-cooling tube ground into its neck, with 25 cc. of the chromate solution and the same volume of normal sulphuric acid. Heated to gentle boiling, the time necessary for the complete reduction of the chromate varies much with the fineness of division of the silver. With silver used in the first two experiments the reduction was complete in fifteen minutes, while that used in 3, 4, and 5 required much longer. After the reduction was complete, the remaining silver was weighed in a Gooch crucible.

Following are the results of five experiments. The theoretical value is, of course, based upon the supposition that 1 molecule of chromate oxidizes 6 atoms of silver.

	Volume of bichromate. cc.	Silver dissolved.	Theory.
1	25.00	0.5413	0.5397
2	25.00	0.5428	.....
3	25.00	0.5380	.....
4	25.00	0.5366	.....
5	25.00	0.5376	.....

Action of Silver on Iodic Acid.—In experiment 6 the iodic acid and silver were heated with normal sulphuric acid and in 7 the iodic acid was in water solution. After heating at the boiling-point for about two hours, replacing the water evaporated from time to time, the undissolved silver, silver iodate and iodide were weighed. So much of the mixture as possible, without getting asbestos from the Gooch crucible, was transferred to a porcelain crucible, weighed and heated to redness. Oxygen was evolved and was determined by loss. From the loss of oxygen in a portion of the mixture, the silver as iodate could be calculated, and from this, the silver in solution and the silver taken, the silver as iodide could also be calculated. In the following, column 1 shows the silver used, 2 the total loss of oxygen, 3 silver as iodate, 4 silver in solution, and 5 silver as iodide.

	1.	2.	3.	4.	5.
6	1.3700	0.1418	0.3188	0.0434	0.0727
7	1.0225	0.1508	0.3390	0.0008	0.0727

In experiment 6, the ratio of silver as iodide to the total silver oxidized is 1:5.98 and in 7 the ratio is 1:5.67.

Action of Silver on Chloric Acid.—In experiment 8, 7 cc. of Merck's chloric acid were diluted to 50 cc., and such a solution was about three-tenths normal. The acid contained only a trace of hydrochloric acid, too small an amount in the volume taken to influence the result. In experiment 9, normal sulphuric acid and pure potassium chlorate were used. After heating about two hours, the silver in solution and the residue of silver and silver chloride were determined.

	Silver taken.	Silver in solution.	Silver as chloride.
8	2.0295	0.8859	0.1775
9	1.9517	0.5514	0.1473

In experiment 8, the ratio of the silver as chloride to the total silver acted upon is 1 : 5.99 and in 9 the ratio is 1 : 4.74.

The experiments show that both chromic and iodic acids are capable alone of oxidizing large quantities of finely divided silver. Both acids seem to react quantitatively upon silver with the result that a molecule of the acid is completely reduced and 6 atoms of silver are oxidized, 1 of which forms a halide and 5 form silver chlorate or iodate as shown in the equation

$$6Ag + 6HClO_3 = AgCl + 5AgClO_3 + 3H_2O.$$

The action goes on in very dilute solutions. Calculations from the amounts of acids used and silver oxidized show that the strength of the iodic acid solution, when the experiment was stopped in experiment 7, could not have exceeded one-twentieth normal, and the strength of the chloric acid at the end of experiment 8 was about one-tenth normal. Bromic acid also readily dissolves silver but this reaction has not yet been quantitatively studied.

Action of Dilute Sulphuric Acid on Silver.—M. Carey Lea[1] has stated that even very dilute sulphuric acid dissolves, in small quantity, finely divided silver. I found this to be true in the case of every sample of silver prepared, and the amounts dissolved by the normal acid alone were determined. The weights of silver dissolved were in two samples about 0.4 milligram for each gram of silver taken, amounts so small that no corrections were made in experiments 1 to 8. A correction was, however, applied in experiment 9 in which the silver used was much more soluble.

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[1] *Loc. cit.*

Since it was observed that continued heating did not seem to influence the amount of silver which the acid alone dissolved, a study was made of the reason for this solvent action. About a gram of silver on which the acid exerted a marked solvent action, was placed in a hard glass tube which was stoppered into a distilling flask so that the tip of the tube was in the bulb of the flask.

Through the tube and flask, which contained normal sulphuric acid and was placed horizontally, was passed pure hydrogen and the acid was boiled to expel any dissolved oxygen. The silver was heated in the current of hydrogen to reduce any oxide that it might contain. When cool it was allowed to fall into the boiling acid by tilting the flask and tube. By depressing the neck of the flask, small portions of the acid could be drawn off through the side tube from time to time and tested for silver. Though the evaporation was continued practically to dryness, no trace of silver was found in solution.

To determine whether the apparent solvent action might not be due to superficial oxidation of the silver, the above experiment was repeated, save that the silver was not heated. Again after long boiling no silver was found in solution. It then seemed of interest to determine at least approximately at what concentration boiling sulphuric acid begins to attack silver. The experiment was repeated save that the silver was not heated, and pure, dilute acid of the ordinary reagent strength was used. The acid was allowed to concentrate by evaporation and was, toward the end of the experiment, tested for silver at least every minute. Suddenly the character of the boiling changed and the silver rose to the surface and appeared spongy, owing to the formation of sulphur dioxide. The boiling was stopped and a test showed silver in solution. The acid was allowed to cool, a portion of it was weighed and titrated, and it showed a concentration of 74.03 per cent.

The above experiment seems to show definitely that dilute sulphuric acid alone is incapable of dissolving finely divided silver, and that the seeming solvent action is due to the oxygen of the air, oxygen dissolved in the acid, or to that derived from some external source.

In the near future an attempt will be made to ascertain whether, by excluding extraneous oxygen, the actual oxidizing power of a bichromate solution may not be very accurately determined with silver.

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REDUCIBILITY OF SOME METALLIC OXIDES BY HYDROGEN AND CARBON MONOXIDE.

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IN passing hydrogen gas over silver oxide in a bulb tube to show the reduction of the oxide to metallic silver I frequently noticed slight explosions and a sudden change of oxide to metal at what seemed a low temperature for such an effect. In the literature, I found that silver oxide was reduced by hydrogen at 85°[1] and 100°.[1] Wishing to test the accuracy of these temperatures, the following investigation was begun with the impression that both temperatures were too high. Both hydrogen and carbon monoxide were used to reduce the silver oxide. Later, other oxides were submitted to the reducing action of these two gases.

The method used by Mueller[2] consisted in placing a glass tube containing the oxide in the sand of a sand-bath. A thermometer was thrust into the sand so that the bulb was close to the part of the tube containing the oxide. The tube was bent at a right angle, one end sealed, the open lower end dipping under water. The tube was filled with hydrogen and the temperature increased. Reduction of the oxide was shown by ascent of water in the open end or arm of the tube.

Wright[3] and Luff placed the metallic oxides for reduction in a test-tube arranged vertically in a paraffin bath, about 0.5 gram being taken for each observation. The mouth of the test-tube was closed by a cork with three perforations, one for the thermometer, the bulb of which reached to the bottom of the tube, one for the entrance tube for leading in the pure gas, and the third for an exit tube just passing through the cork and bent at a right angle and coupled by a rubber joint to a Will and Varrentrapp's ammonia

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[1] Wöhler: *Ann. Chem.* (Liebig), **30**, 4.

[2] Müller: Pogg. *Ann.*, **136**, 51.

[3] *J. Chem. Soc.* (London), **33**, 1.