The fact adduced by him that, under certain conditions, cuprous sulphide may be formed by the action of the metal upon sulphuric acid does not allow any conclusions to be drawn respecting the presence of "nascent" hydrogen, since it may be explained perfectly well, either by the direct reducing action of the copper or by Traube's theory, which is backed up by *almost* convincing evidence.[1]

Stannous chloride will reduce sulphuric acid with formation of hydrogen sulphide, sulphurous acid and free sulphur: an analogous reaction in which the assumption of "nascent" hydrogen is inadmissible.

I hope to complete before long another series of experiments, now under way, which will form in a future communication a further contribution to the subject of the present paper.

THE OXIDATION OF SILVER.

BY CHARLES E. WAIT.

Received January 17, 1896.

IN a former paper[2] I had occasion to call attention to the large amount of silver present in a sample of bismuth litharge from a western smelting and refining company. The silver in this instance estimated in the metallic state was 2.94 per cent.

There was some doubt expressed as to the condition in which the silver existed, it being usually reported in the metallic state. Upon investigation it was found, as was shown in the paper referred to, that the silver did not exist wholly in the metallic state, but partly in another form, probably the oxide.

The conclusions reached at that time were based upon the following experiments:

1. A weighed sample of the litharge was boiled in acetic acid for about half an hour, the solution was filtered, and the filtrate gave no reaction for silver.

2. Same as above, but with continued boiling, the filtrate gave no reaction for silver.

3. A sample was placed in cold acetic acid, kept there for half an hour, then heated to boiling, the solution was filtered, the lead was precipitated, and in the filtrate silver was found to exist, corresponding to 19.25 per cent. of the silver in the litharge. Other determinations gave closely agreeing results, and

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[1] Moritz Traube, *loc. cit.* and *Ber. d. chem. Ges.*, 18, 1877.

[2] Trans. Am. Inst. Min. Eng., 15.

it is interesting to note that the residues contained grains of metallic lead, or argentiferous lead.

I have placed the following interpretations upon the above results:

In Nos. 1 and 2 if any silver in any form was dissolved in the acetic acid, it was in turn reprecipitated by boiling, in the presence of metallic lead.

In No. 3 the silver dissolved, did not in all probability exist in the metallic state ; and in this case was not precipitated by the lead, or argentiferous lead, the solution being brought merely to the boiling temperature.

I have been led to the above interpretations by showing that neither metallic silver reduced to fine subdivision by mechanical means, nor silver freshly prepared by zinc from silver chloride is soluble in acetic acid, while argentic oxide is soluble in that acid ; and a solution of silver oxide in acetic acid was precipitated completely by metallic lead upon boiling.

If the oxides are decomposed at a temperature of 300° C.,[1] or less,[2] how may we account for the existence of this substance in a product so highly heated as the litharge from the refining furnace?

Berthier[3] has observed that lead may be oxidized by oxide of copper, when melted together, and further consideration of the subject shows that certain metals may be oxidized by being melted with an oxide of another metal, this oxidation depending in all probability upon the excess of the oxide present. Silver does not appear to be oxidized by oxide of copper if the results in experiment No. 18 are trustworthy.

According to Fournet's experiments[4] silver is not an exception to the metals to which litharge gives up a part of its oxygen when fused with them for a considerable time.

While it is true that in the process of cupellation there is a loss of silver due possibly to oxidation, yet I do not find any losses even in the most exaggerated cases at all comparable with the percentages of silver oxide which I have been able to produce by a simple, yet possibly new, method.

It seemed to me an interesting problem to ascertain, if possible, the conditions under which silver may be oxidized at a high

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[1] Roscoe and Schorlemmer, Vol. II, Part I.

[2] *J. Chem. Soc.*, 65, 316.

[3] Crookes and Rohrig, Metallurgy.

[4] Erdman's Journal.

temperature, and the conditions under which the oxide of silver, if thus formed, would remain as such.

Some interesting work has been done along a similar line,[1] that is, a study of those oxides which are stable at high temperature, and those which are decomposed, but under neither head does silver seem to have been discussed.

So few observations have been made along this exact line, as far as I have seen, that I have been induced to make some investigations with a view to throw light upon the subject, if possible.

The general method of conducting the experiments, I will briefly state as follows: Metallic silver in minute subdivision was incorporated with one of the several bodies mentioned below, this mixture was put in a cupel of bone ash, or in a scorifier, and then placed in the muffle of an assay furnace and subjected to an oxidizing heat.

After this operation the mass was removed to a mortar, pulverized, then digested with acetic acid to boiling, the solution was filtered; in case a lead compound had been used, the lead was removed by sulphuric acid, hydrochloric acid was then added. The silver chloride thus formed was filtered, dried, and wrapped in least pure lead foil and then carefully cupelled.

There was thus obtained the silver, which was converted to argentic oxide,—at least I assume it to be such,—and it is interesting to note that the amount of silver converted to oxide, and tabulated below, shows a very great range, in fact from only a trace to as much as thirty-nine per cent. of the silver used.

This variation seems dependent upon a number of conditions, namely: the body with which the silver was mixed, duration and condition of heat, whether low, medium, or high temperature. As I did not use a pyrometer to ascertain the temperature during these experiments, I have thought it desirable to indicate the degree of heat approximately by such terms as "low," "medium," and "high," referring to the condition of the heat as usually obtained in the muffle in the assay of silver.

I append herewith several tables of experiments and results:

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[1] *J. Chem. Soc.*, April, *1894*.

TABLE A.

No. experiment.	Ag in gram.	Heated with.		Time of heat.	Condition of heat.	Per cent. Ag. as Ag_2O.
1	0.5	2.5 grams	MnO_2.	60 min.	medium	9.40
2	0.5	5.0 "	MnO_2.	60 "	"	7.78
3	0.5	2.5 "	Fe_2O_3.	60 "	"	none.
4	0.5	2.5 "	Bi_2O_3.	60 "	"	"
5	0.5	2.5 "	ZnO.	60 "	"	"
6	0.5	2.5 "	$CaCO_3$.	60 "	"	"

From the above it will be seen that silver oxide was produced, and remained as such where manganese dioxide was used and in no other case; it would also seem that this oxide was made at the expense of the manganese dioxide and not by atmospheric oxidation, nor does it seem to have been produced in experiment 3, (certainly not remaining as such) assuming the possible conversion of Fe_2O_3 to Fe_3O_4.[1]

TABLE B.

No. experiment.	Ag. in gram.	Heated with.		Time of heat.	Condition of heat.	Per cent. Ag. as Ag_2O.
7	0.5	7.5 grams	MnO_2.	30 min.	medium.	34.16
8	0.5	10.0 "	MnO_2.	30 "	"	18.84
9	0.5	3.0 "	$CaCO_3$.	60 "	"	none.
10	0.5	3.0 "	Fe	60 "	"	"

The above results show that silver oxide was produced in the presence of manganese dioxide only; that less duration of heat than in Table A gives the amazingly large per cent. of that oxide, and it furthermore seems that the oxide produced is not in proportion to the manganese dioxide used, but the reverse condition is generally seen in each set of experiments.

TABLE C.

No. experiment.	Ag. in gram.	Heated with.		Time of heat.	Condition of heat.	Per cent. Ag. as Ag_2O.
11	0.5	1 gram	MnO_2.	2.5 min.	high.	32.24
12	0.5	2 grams	MnO_2.	2.5 "	"	34.28
13	0.5	2 "	MnO_2.	20 "	"	11.72

The above experiments show, other conditions being the same, the longer the duration of the heat the less oxide there is produced.

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[1] *J. Chem. Soc.*, 65, 313.

TABLE D.

No. experiment.	Ag. in gram.	Heated with.	Time of heat.	Condition of heat.	Per cent. Ag. as Ag_2O.
14	0.5	5 grams PbO.	10 min.	medium.	38.85
15	0.5	4 " PbO_2.	10 "	"	35.12
16	0.5	2 " BaO_2.	5 "	"	12.28
17	0.5	7 " BaO_2.	10 "	high.	2.04
18	0.5	4 " CuO.	12 "	"	none.

In Nos. 14 and 15 the mixtures were placed in scorifiers, and covered with ten grams of lead oxide.

In Nos. 16 and 17 the mixtures were placed in cupels and covered with two grams of barium dioxide.

It is interesting here to notice that barium dioxide serves as an oxidizing agent; that the amount of silver oxide produced decreases probably both with increase of time and temperature.

Although lead dioxide may readily give up a part of its oxygen and thereby be converted into a lower oxide, yet the amount of silver oxide produced was no greater than with lead oxide alone; this is an interesting illustration of the property of lead oxide to serve as a possible carrier of atmospheric oxygen, producing silver oxide in a manner similar to that of the two bodies. manganese dioxide and barium dioxide, liberating oxygen. In the case of lead oxide, No. 14, if dissociation is not possible[1] even at so high a temperature as 1750° C, it seems most reasonable to account for its peculiar oxidizing action, as mentioned above; *viz.*, as a carrier of atmospheric oxygen. Although copper oxide has been shown to yield up a part of its oxygen at 1500° C. yet I find no evidence of silver oxide existing in experiment 18 in the remaining ignited mass.

TABLE E.

No. experiment.	Ag_2O. in gram.	Heated with.	Time of heat.	Condition of heat.	Per cent. Ag. as Ag_2O.
19	0.5 Ag_2O.	5 grams MnO_2.	60 min.	medium.	36.4
20	0.5 Ag_2O.	3 " Fe.	60 "	"	0.3
21	0.5 Ag_2O.	3 " $CaCO_3$.	30 "	"	0.2

In Table E a variation was made in the nature of the experiment. Freshly prepared silver oxide was used; while this oxide was completely decomposed upon being heated gently upon a porcelain lid, yet in No. 19 where manganese dioxide

[1] *J. Chem. Soc.*, 65, 316.

was used, it will be seen that 36.4 per cent. of this silver oxide completely escaped decomposition.

The above results, in connection with others along a similar line, have induced me to believe that attention has not heretofore been directed to the ease with which silver may be oxidized by lead oxide, and particularly by substances which give up a part of their oxygen upon gentle ignition, such as manganese dioxide and barium dioxide. Is it not then reasonable to assume that certain losses, or irregularities in the treatment of silver and its compounds, may be due to this cause?

UNIVERSITY OF TENNESSEE.

THE DETERMINATION OF THE SOLID FAT IN ARTIFICIAL MIXTURES OF VEGETABLE AND ANIMAL FATS AND OILS.

BY J. H. WAINWRIGHT.

Received February 1, 1896.

IT will readily be conceded by most analysts that there is no subject in analytical chemistry presenting more difficulties than the examination and analysis of the fixed oils and fats. This is especially true in the case of mixtures of oils of different origin, and there is probably no problem more difficult to solve in most cases than the analysis of such a mixture when even approximately correct quantitative results are required.

It is only within a comparatively recent period that the investigations of the chemist have been especially directed to this branch of research as formerly the character and identity of a sample of unknown origin was chiefly, but very doubtfully, established by means of obscure color reactions and one or two simple determinations, such as specific gravity, melting point, etc.

At present, however, the investigations of many learned chemists have shown that determinations of the chemical and physical properties of a sample, such for example as the combining weight of fatty acids, the percentage of iodine the sample will absorb, the percentage of volatile fatty acids, etc., will yield results by which may be established, in most cases with reasonable accuracy, the fact as to whether it is a simple oil or fat, such as olive, linseed, lard, butter, etc., and if so its iden-