solution of ammonium acetate until it was evident that all of the thorium phenylarsonate was precipitated, after which the mixture was digested on a hot plate for about ten minutes. The precipitate was then filtered off, washed, dissolved in 30 cc. of 1:1 hydrochloric acid, the solution diluted to about 300 cc. and treated with a little sulfurous acid. The thorium was reprecipitated by adding a few cubic centimeters of phenylarsonic acid, 75 cc. of acetic acid and enough ammonium acetate to insure complete precipitation.

This last precipitate was then dissolved in 30 cc. of 1:1 hydrochloric acid, the solution treated with 5 g. of oxalic acid and the whole diluted to about 200 cc. This was allowed to stand for at least 12 hours. Results of 6.54, 6.52, 6.50% of thoria equivalent were obtained by this method compared with an average of 6.48 by the pyrophosphate method.[3]

Summary

Zirconium phenylarsonate is an extremely insoluble substance, eminently suited for the separation of zirconium from all elements except hafnium. It has been shown that it can be quantitatively precipitated from both hydrochloric acid and sulfuric acid solutions.

Thorium phenylarsonate differs from the phenylarsonates of the rare earths, being insoluble in solutions containing large amounts of acetic acid. A method is given for the determination of thorium in monazite sand.

The authors highly recommend this reagent for the quantitative determination of zirconium and thorium.

Work is being continued with regard to the quantitative estimation of hafnium by this reagent.

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PREPARATION OF DISILICON HEXACHLORIDE

BY JOSEPH B. QUIG WITH JOHN A. WILKINSON

Introduction

In reviewing the methods that have been proposed for the preparation of disilicon hexachloride,[1] that proposed by Martin seemed the best. Gattermann and Weinlig chlorinated metallic silicon at 300° and obtained a yield of 20% but this could not be duplicated in this Laboratory. Martin

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[3] Carney and Campbell, THIS JOURNAL, **36**, 1134 (1914).

[1] (a) Friedel, *Compt. rend.*, **73**, 1011 (1871). (b) Troost and Hautefeuille, *Ann. chim. phys.*, [5] **7**, 453 (1876). (c) Gattermann and Weinlig, *Ber.*, **27**, 1943 (1894). (d) Gattermann and Ellery, *Ber.*, **32**, 1114 (1899). (e) Besson and Fournier, *Compt. rend.*, **148**, 839 (1909); (f) **149**, 34 (1909). (g) Martin, *J. Chem. Soc.*, **105**, 2836 (1914). (h) Stock, Brandt and Fischer, *Ber.*, **58**, 648 (1925).

chlorinated 50% ferrosilicon at 180–200° and obtained a yield of 5.25%, calculating the percentage on the basis of the total chlorides condensed. If the percentage is calculated on the basis of the ferrosilicon used, the yield is 2.5%.

Gattermann and Weinlig assumed that the chlorination gave silicon tetrachloride first and that this was then reduced by more silicon to disilicon hexachloride. Martin, on the other hand, says that the silicon tetrachloride is the final product and disilicon hexachloride the intermediate compound. In proof of this he has shown that the reaction, $3SiCl_4 + Si = 2Si_2Cl_6$, does not take place to any appreciable extent when silicon tetrachloride vapor is passed over metallic silicon or ferrosilicon between 200° and 300°. He has also shown that the reaction, $Si_2Cl_6 + Cl_2 = 2SiCl_4$, does not take place unless the tube through which the vapors are passing reaches the boiling point of disilicon hexachloride (144°) when it reacts slowly, but at 300° it reacts very rapidly.

Martin believes, therefore, that the reason ferrosilicon gives a higher yield of disilicon hexachloride than does pure silicon is simply because the ferrosilicon chlorinates at a lower temperature and there is less tendency for the disilicon hexachloride which is first formed to go to silicon tetrachloride at this lower temperature. He gives no explanation as to why the ferrosilicon chlorinates at a lower temperature.

A supply of disilicon hexachloride was wanted for some other experiments and an endeavor was made to increase the yield obtainable by Martin's method. Since the effect might be thought to be due to the ferric chloride acting in its role as a chlorine carrier, an intimate mixture of pulverized silicon and iron powder was chlorinated at 200° but no silicon chlorides were formed although the iron reacted violently enough to glow and formed a large amount of ferric chloride. Silicon chlorides began to form only when the temperature was raised to 300°. This shows that the presence of ferric chloride is not the cause of the lowering of the temperature at which the silicon in ferrosilicon chlorinates.

In spite of the fact that Martin[1g] has shown that silicon tetrachloride is not reduced to lower chlorides by metallic silicon at the temperature at which ferrosilicon can chlorinate to disilicon hexachloride, it was thought that passing a mixture of chlorine and silicon tetrachloride over ferrosilicon might yield disilicon hexachloride. There were three reasons for this view. (a) If disilicon hexachloride is formed first and this is then chlorinated to silicon tetrachloride the presence of the latter, one of the products of the reaction, would tend to retard the final chlorination. (b) The silicon tetrachloride would dilute the chlorine and thus retard the rate of final chlorination. (c) The silicon tetrachloride would act as an inert gas and tend to sweep the lower chloride away from the point where the temperature was high enough to allow the final chlorination to take place.

The iron in the ferrosilicon reacts readily with chlorine and being mixed very intimately with the silicon, either as a compound or solid solution, some of the silicon would be heated locally by the glowing iron to a temperature high enough to cause it to chlorinate to the lower chlorides. These would be swept on by the silicon tetrachloride vapor to a cooler portion of the tube, where they would be stable and not chlorinate further.
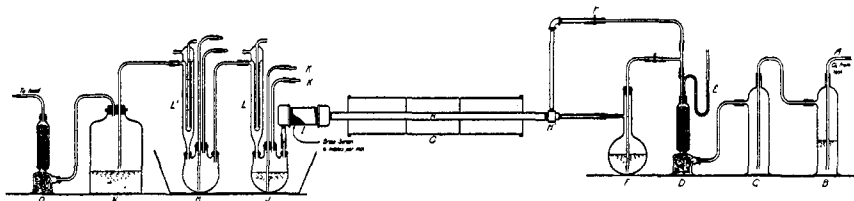

Fig. 1.—Chlorination apparatus.

The above theory was tested by passing mixtures of silicon tetrachloride and chlorine of different concentrations and at different rates over ferrosilicon heated to 200°. The vapor mixtures were made by passing chlorine gas through liquid silicon tetrachloride before passing it over the ferrosilicon. By varying the temperature of the liquid silicon tetrachloride its concentration in the vapor phase could be changed.

The apparatus shown in Fig. 1 was similar to that used by Martin with a few changes.[2] The main difference was the use of the flask to saturate
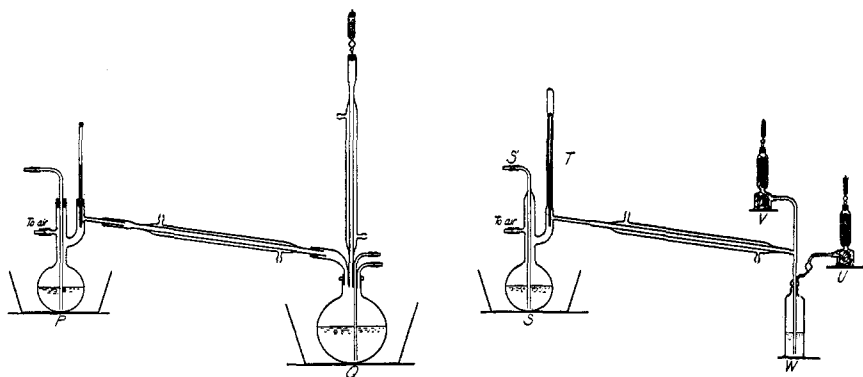

Fig. 2.—Distillation apparatus.

the chlorine with silicon tetrachloride and the introduction of a ferric chloride trap I which was an enlarged iron pipe containing a brass screen to prevent the ferric chloride from entering the flask J in which the silicon chlorides were condensed.

The liquid chlorides were removed from the flask J by applying air pressure to the tube K' which forced the liquid into the all-glass distill-

[2] Ref. 1g, p. 2846.

ing system shown in Fig. 2 where the disilicon hexachloride and trisilicon octachloride were separated from the large amount of silicon tetrachloride by fractional distillation. Final purification was made in the same way, the disilicon hexachloride coming over between 144° and 145° and the small amount of trisilicon octachloride at 213°.

Analysis of Disilicon Hexachloride

Small glass bulbs with capillary tubes were blown and thoroughly dried by heating in a flame. The sample was taken by inserting the capillary tube of a weighed bulb below the level of the liquid disilicon hexachloride; by alternately heating and cooling the bulb a sample of from 0.1500 to 0.2000 g. could be drawn into the bulb which was then sealed and weighed.

The bulb and sample were then transferred to a heavy-walled bottle containing 100 cc. of 0.1 N sodium hydroxide solution and after this bottle had been tightly stoppered it was shaken vigorously. The following reaction[1h] takes place: $Si_2Cl_6 + 10NaOH = 6NaCl + 2Na_2SiO_3 + 4H_2O + H_2$. After the reaction was complete the solution was diluted and an aliquot portion analyzed for the chlorine by the Volhard method. The calculated percentage of chlorine is 78.99. Three results were 78.92, 78.83 and 78.88%.

Data

The results obtained are shown in Table I. The concentration of the silicon tetrachloride in the vapor was varied by changing the temperature of the liquid silicon tetrachloride. The rate of flow was varied by changing the chlorine pressure. The percentage of disilicon hexachloride is calculated on the basis of the weight of silicon used from the 50% ferrosilicon added. This weight was obtained by washing out the reacting tube with water and weighing the undecomposed ferrosilicon and subtracting this

TABLE I

YIELDS OF DISILICON HEXACHLORIDE FROM FERROSILICON WITH CHLORINE AND SILICON TETRACHLORIDE

	1	2	3	4	5	6
Time, min..............	720	540	750	720	270	270
Temp. of liquid SiCl₄, °C.	0	0	25	25	25	25
Ferrosilicon added, g.....	450[a]	250	450	450	450	450
Ferrosilicon used, g......	102	76	140	130	105	127
SiCl₄ aspirated, g........	83.4	108.9	372.6	370.9	343.78	564.9
SiCl₄ asp. per min., g. ...	0.1158	0.2016	0.4968	0.5152	1.2713	2.092
Lower chlorides formed, g.	49.4	58.9	114	108	66.4	67.1
Lower chlorides equiv. to Si used, g............	242.7	180.8	331.1	309.3	249.8	302.2
Lower chlorides formed, %..................	20.3	32.6	34.2	34.9	26.6	22.3

    [a] When 450 g. was used two furnaces were run in parallel.

weight from the total ferrosilicon added. The weight of the lower chlorides, most of which was disilicon hexachloride, was found from the residue after distilling out the silicon tetrachloride.

An inspection of the table shows that the yield of lower chlorides can be greatly increased by the addition of silicon tetrachloride to the chlorine up to a certain point. Beyond that, a further addition reduces the yield which indicates that the first increase is due to a retarding of the final chlorination and not to the reduction of silicon tetrachloride by silicon.

The authors are indebted to the Chemical Warfare Service for the supply of silicon tetrachloride used.

Summary

1. The ferric chloride formed by the chlorination of a mixture of iron and silicon does not act as a catalyst to increase the yield of lower chlorides of silicon nor to lower the temperature at which silicon is chlorinated.

2. The yield of disilicon hexachloride can be increased by passing silicon tetrachloride with chlorine over ferrosilicon heated to 200°.

3. This increase is due to the retarding of the final chlorination of disilicon hexachloride to silicon tetrachloride and not to the reduction of the latter by silicon.

AMES, IOWA

BASIC STANNOUS SULFATE

BY C. M. CARSON

It is well known that water decomposes stannous salts with the formation of basic salt precipitates and that sodium hydroxide forms similar precipitates from solutions containing stannous ion. The composition of the precipitates for stannous chloride has been determined by Carson[1] and it seemed desirable that the basic salts of stannous sulfate should likewise be examined.

The stannous sulfate samples obtained from two prominent American manufacturers contained such a large amount of insoluble material that they were quite unsuitable either for direct use or as raw material for the manufacture of a pure product. A good quality of the salt may be made from tin and sulfuric acid but the following method is better for small scale operation.

About 25 g. of cupric sulfate is added to 200 cc. of water and 10 cc. of sulfuric acid in a 500cc. flask, and after the solution has been heated to boiling, small fragments of tin foil are dropped in, until 20 to 25 g. has been used. With continued boiling, the

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[1] Carson, THIS JOURNAL, **41**, 1969 (1919).