CCLXVI.—*Researches on Silicon Compounds. Part VI. Preparation of Silicon Tetrachloride, Disilicon Hexachloride, and the Higher Chlorides of Silicon by the Action of Chlorine on 50 per cent. Ferrosilicon, Together with a Discussion on Their Mode of Formation.*

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THE method once exclusively used for preparing silicon tetrachloride in the laboratory was Oersted's process (*Ann. Phys. Chem.*, 1825, [ii], **5**, 132) of passing chlorine over a red-hot mixture of silica and carbon.

A great improvement was introduced by Gattermann and Weinlig in 1894 (*Ber.*, 1894, **27**, 1943; see also Gattermann and Ellery, *Ber.*, 1899, **32**, 1114), when they passed chlorine over crude silicon contained in a glass tube heated to 300—310°. They obtained by this process a product containing 80 per cent. of silicon tetrachloride, 20 per cent. of disilicon hexachloride, Si_2Cl_6, and 0·5 to 1 per cent. of trisilicon octachloride, Si_3Cl_8.

Up to the present time this has proved by far the easiest method of preparing, not only silicon tetrachloride, but also disilicon hexachloride and the higher chlorides of silicon.

The cost, however, of preparing disilicon hexachloride in quantity by this method is almost prohibitive, and consequently disilicon hexachloride is sold at an extremely high price.

As some kilos. of this costly product were necessary in order to carry out some of the research work on which the author is engaged, it became necessary to devise some cheap and convenient method of preparing disilicon hexachloride in quantity.

After much preliminary work it was found that commercial 50 per cent. ferrosilicon, such as is used for refining steel, can be used instead of the expensive silicon itself for the purpose of preparing disilicon hexachloride in quantity, and that this material forms by far the most economical known method of preparing silicon tetrachloride.

In fact there can be no doubt that, in future, 50 per cent. ferrosilicon must prove the starting point for the preparation of all chlorinated compounds of silicon.*

Consequently, a description of the method of using this material for preparing silicon tetrachloride, disilicon hexachloride, and the other chlorides of silicon, will be of some value to other workers on silicon compounds, as the optimum conditions were only arrived at after much troublesome experimenting and many preliminary failures.

In order to give some idea of the extent to which the difficulties attached to the preparation of these highly hygroscopic liquid chlorides of silicon were overcome by means of the final form of apparatus described below, the author may state that he succeeded in isolating 3 kilos. of pure disilicon hexachloride, 200 grams of trisilicon octachloride, and more than 54 kilos. of pure silicon tetrachloride by passing 143 kilos. of chlorine over 50 kilos. of ferrosilicon. This was done in an ordinary chemical laboratory, and all leakage of chlorine and of the volatile silicon tetrachloride was so completely overcome in the final stages of this preparation that ordinary class work went on around the apparatus while the preparation was actively proceeding.

Since water causes the instant decomposition of these chlorides, all traces of atmospheric moisture must be carefully excluded from all parts of the apparatus, and it is this necessity that makes their preparation a matter of so much trouble.

The large amount of disilicon hexachloride prepared by this process enabled the author to obtain it in a state of very great purity, and so he was able to investigate its properties more carefully than was possible with earlier workers. It was found, for example, that Gattermann and Weinlig's value for the boiling point of disilicon hexachloride, Si_2Cl_6, namely, 145—146°, was undoubtedly a little too high, the true boiling point being 144—145·5°/760 mm. The boiling points of the substance under

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* The silicon purchased as 50 per cent. ferrosilicon is nearly eighteen times cheaper than when purchased as pure silicon; moreover, 50 per cent. ferrosilicon is readily available, the other grades being made only on the small scale.

pressures ranging from 12 mm. to ordinary atmospheric pressure were also accurately determined. They are tabulated on p. 2852.

The density of pure disilicon hexachloride was found to be D_4^{15} 1·5624; Troost and Hautefeuille gave D 1·58.

The refractive index for sodium light (*D* line) was found to be 1·4748 at 18°. Gattermann and Weinlig (*loc. cit.*) give the refractive index for "red light" as 1·45.

It was also shown that although at the ordinary temperature disilicon hexachloride does not combine with chlorine (although the latter is very soluble in it), yet at about 300° it takes fire in this gas and burns to silicon tetrachloride, thus, $Si_2Cl_6 + Cl_2 = 2SiCl_4$.

This is a new fact of considerable importance, since it throws light on the mode of formation of disilicon hexachloride by the action of chlorine on silicon or ferrosilicon (see below).

Although Gattermann and Weinlig (*loc. cit.*) showed that when water acts on disilicon hexachloride there is produced silico-oxalic acid, $(SiO_2H)_2$, yet they seem to have overlooked the fact that there are also soluble colloidal forms of silico-oxalic acid produced at the same time, as the author proved in the course of this work. These colloidal forms are to be investigated.

After the disilicon hexachloride had distilled, about 200 grams of crude trisilicon octachloride passed over. This, after careful fractionation, yielded about 150 grams of pure octachloride, which boiled at 210—213° under atmospheric pressure (Gattermann and Weinlig, *loc. cit.*, give 210—215°, and Besson and Fournier, *Compt. rend.*, 1909, **148**, 840, give 215—218°. This value is undoubtedly too high). However, it was shown that trisilicon octachloride gradually decomposed when distilled under the ordinary pressure, giving rise to a dark-coloured residue. To avoid decomposition it was found advisable to distil it under diminished pressure. It could be repeatedly distilled without decomposition at pressures below 110 mm. (when it boiled at about 149°). Trisilicon octachloride is considerably less stable than disilicon hexachloride. The density is D_4^{15} 1·61, and the refractive index (*D* line) 1·5135 at 14·5°.

After the trisilicon octachloride had been removed the liquid remaining was fractionated under greatly diminished pressure, and higher chlorides were isolated in small quantities. These were decomposed by water, giving rise to white, amorphous products, which dissolved in alkalis with the evolution of hydrogen. A later communication will be made on this subject. Besson and Fournier (*Compt. rend.*, 1909, **148**, 839; **149**, 34) recently described higher chlorides, which were isolated by a different method.

The residues left after removal of these chlorides consisted of (*a*) about 13 grams of a viscid, black, tar-like mass and (*b*) about 160 grams of a black powder like animal charcoal. These products are now being investigated.

It is thus shown that the product obtained by the action of chlorine on silicon and ferrosilicon is no simple substance, but a very complex mixture of silicon compounds, the different components of which are now in process of isolation.

Gattermann and Weinlig (*loc. cit.*) explained the formation of disilicon hexachloride when chlorine passes over silicon at 300° by assuming that the chlorine first directly unites with the silicon to form silicon tetrachloride, thus:

$$Si + 2Cl_2 = SiCl_4.$$

Next they supposed that the silicon tetrachloride thus formed at once reacts with more silicon to produce the hexachloride, thus:

$$3SiCl_4 + Si = 2Si_2Cl_6.$$

For the last twenty years this explanation of Gattermann and Weinlig has been universally accepted as the correct one. However, this explanation is certainly quite erroneous for the simple reason that at the low temperatures employed by Gattermann and Weinlig, and also by the author in the preparation of disilicon hexachloride by the action of chlorine on ferrosilicon, silicon tetrachloride does not react with silicon to produce disilicon hexachloride in noticeable quantity. This is conclusively shown in the experiments quoted below. Gattermann and Weinlig made not the slightest attempt to verify their theory experimentally. Indeed, on theoretical grounds this formation at a low temperature of disilicon hexachloride from silicon and silicon tetrachloride would appear to be most improbable since disilicon hexachloride is an endothermic compound, and its formation requires the absorption of a considerable amount of heat.

A white heat would favour its formation (as in the similar case of nitric oxide), but a low temperature would not be expected to act in this way. Troost and Hautefeuille showed that at a temperature approaching the fusing point of porcelain (that is, at a white heat) the formation of disilicon hexachloride from silicon and silicon tetrachloride does take place to a limited extent (*Ann. Chim. Phys.*, 1876, [v], **7**, 459), but the conditions under which the formation takes place in Troost and Hautefeuille's experiments are entirely different from those under which it occurs in Gattermann and Weinlig's experiments, where the temperature is kept quite low, and also in the author's experiments, whereby disilicon hexachloride is produced by the action of chlorine on ferrosilicon, where also only low temperatures are employed, so that arguments derived from Troost and Hautefeuille's experiments do not apply in any way to the case now under consideration.

The problem to be explained is how a large proportion, amounting to something like 20 per cent. of disilicon hexachloride, is produced by the action of chlorine on silicon at the low temperatures (about 300°) employed by Gattermann and Weinlig.

The conclusive refutation of Gattermann and Weinlig's theory is given by the following experimental facts established by the author.

(1) When silicon tetrachloride is distilled over either silicon or ferrosilicon heated to any temperature between 200° and 340° no noticeable amounts of disilicon hexachloride can be detected in the resulting silicon tetrachloride; in other words, disilicon hexachloride is not formed by the action of silicon tetrachloride on silicon at moderately low temperatures, as Gattermann and Weinlig supposed.

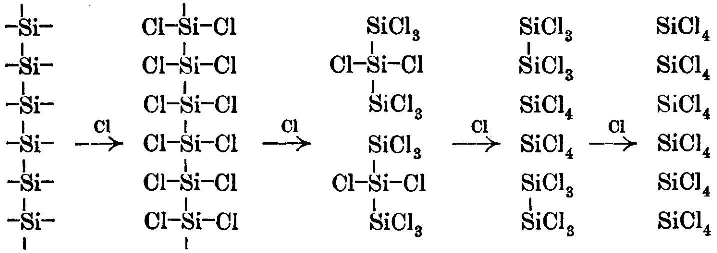
(2) Silicon tetrachloride was prepared by allowing chlorine to act on ferrosilicon at one end of a long tube packed with ferrosilicon, and the silicon tetrachloride thus produced was passed over the long length of heated ferrosilicon in the later portions of the same tube. Less disilicon hexachloride was found to be present in the resulting silicon tetrachloride than when only short lengths of ferrosilicon were used. According to the Gattermann and Weinlig theory, the longer the length of ferrosilicon traversed by the vapour of the silicon tetrachloride the better would be the opportunity for the reaction, $3SiCl_4 + Si = 2Si_2Cl_6$, to proceed, so that an increased yield of disilicon hexachloride should have resulted.

(3) Moreover, the lower the temperatures employed the higher the yield of disilicon hexachloride. For example, when the tubes containing ferrosilicon were kept at 180—200°, in some cases more than 8·6 per cent. of disilicon hexachloride was produced; at 250—260° about 4·6 per cent., whilst at 300—310° only about 4 per cent. was obtained. This should not be the case if the Gattermann-Weinlig theory be correct.

It is therefore obvious that some other explanation of the formation of disilicon hexachloride and trisilicon octachloride must be sought for.

The theory now advanced, which explains all the known facts in a satisfactory manner, is the following:

Ordinary silicon (and also the metallic silicides) consists of complex chains of silicon atoms directly united together. The first action of chlorine on silicon (or metallic silicides) is, consequently, a complex one. The chain of silicon atoms is not immediately disrupted by the chlorine, but there are first produced complex chlorinated products still containing chains of silicon atoms directly united. These complex chlorides are then attacked by more chlorine, and decompose into simpler chlorides, such as Si_6Cl_{14}, Si_5Cl_{12}, Si_4Cl_{10}, Si_3Cl_{10}, and Si_2Cl_6, all of which have been isolated. Lastly, the chlorine then attacks these chlorides and produces therefrom silicon tetrachloride. Thus silicon tetrachloride is not the first product of chlorination (as Gattermann and Weinlig supposed), but rather is the final product of chlorination, as indicated in the following scheme:



Chain of silicon atoms in crude silicon.

First stage of chlorination.

Second stage showing how the chain of silicon atoms is broken down by the chlorine.

Third stage showing the production of disilicon hexachloride and silicon tetrachloride.

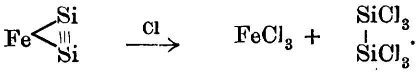
Final stage showing the complete chlorination of the chains of silicon atoms to $SiCl_4$.

Consequently, silicon tetrachloride is the main product of the action, but small quantities of complex chlorides still containing directly linked silicon atoms remain in the silicon tetrachloride, thus indicating its mode of origin.

The amount contained in the silicon tetrachloride of disilicon hexachloride, which possesses only two silicon atoms directly linked, is much greater than the amount of chlorides containing longer chains of silicon atoms, such as trisilicon octachloride, because the longer chains of silicon atoms are the first to be broken under the further action of the chlorine.

The same considerations apply to the case of the metallic silicides, and the fact that silicides, such as 50 per cent. ferrosilicon, can be used for preparing disilicon hexachloride and higher chlorides containing directly linked silicon atoms (see above), may be taken as evidence that in these metallic silicides chains of directly linked silicon atoms are present, and that the small amounts of higher chlorides containing directly linked silicon atoms produced in their chlorination contain parts of the unbroken chains of silicon atoms which were originally present in these silicides, but which have been for the most part broken down, by the further action of chlorine, into silicon tetrachloride.

The formation of disilicon hexachloride from ferrosilicon, for example, would be very simply explained thus:



$$\mathrm{Fe}<\overset{\mathrm{Si}}{\underset{\mathrm{Si}}{|||}} \xrightarrow{\mathrm{Cl}} \mathrm{FeCl_3} + \overset{\mathrm{SiCl_3}}{\underset{\mathrm{SiCl_3}}{|}}.$$

The fact seems definitely established that many of these silicides, such as ferrosilicon, are simply mixtures of complex silicides, and in many cases there is reason to believe that the silicides are not "compounds" at all, but are merely solid solutions of metal in silicon.

The following facts are in favour of this view of the formation of the higher chlorides of silicon:

(1) Complex chlorides of silicon are invariably produced when chlorine acts on silicon or silicides, but (as shown above and below) their formation cannot be accounted for by the action of silicon on silicon tetrachloride.

(2) That the disruption in the presence of chlorine of directly linked silicon atoms, such as exist in disilicon hexachloride, into silicon tetrachloride does actually take place was proved by passing vapours of disilicon hexachloride mixed with chlorine through a tube heated to about 300°, when the disilicon hexachloride caught fire and burnt to silicon tetrachloride, thus: $Si_2Cl_6 + Cl_2 = 2SiCl_4$. It was also proved that at the ordinary temperature disilicon hexachloride does not combine with chlorine to form silicon tetrachloride.

It is therefore practically certain that the small amounts of silicon hexachloride, octachloride, etc., found in the silicon tetrachloride produced by chlorinating silicon or ferrosilicon, are simply the residue or debris of much larger quantities of silicon hexachloride or octachloride originally present, this residue having escaped destruction by the chlorine present owing to the fact that it was quickly removed from the sphere of action of the latter by quick cooling.

(3) This theory also accounts satisfactorily for the fact that the lower the temperature at which chlorine acts on ferrosilicon the greater is the yield of disilicon hexachloride and other chlorides of silicon containing chains of directly united silicon atoms in the molecule.

On the Gattermann-Weinlig theory the reverse effect would rather be expected to take place.

(4) Next to carbon, silicon is the element having the most highly developed power of self-combination. Elementary silicon, therefore, cannot be regarded as a mere aggregate of single silicon

atoms, but rather the element must be thought of as composed of complex molecules consisting of many silicon atoms directly united together, possibly in rings or chains, as in the case of carbon. It would, therefore, appear to be unreasonable to suppose that at the moment the chlorine atoms act on these molecules they immediately fly to pieces with the production of single atoms of silicon, which are then acted on by the chlorine to produce silicon tetrachloride. It is more reasonable to suppose that the chlorination takes place slowly and the whole complex silicon molecule is attacked, forming first complex chloro-compounds, which later, by the further action of the chlorine, break down into simple chlorides, the end-product of the whole complex chain of events being silicon tetrachloride. In this connexion there is the curious experimental fact (see p. 2847) that when chlorine is passed over ferrosilicon heated to a suitable temperature, the formation of silicon tetrachloride does not begin at once. First of all, a period elapses (which may last any time from thirty minutes to one hour, or even, under special and not well-understood conditions, to three hours) during which no silicon tetrachloride at all passes over, but in which it is possible that the surface of the ferrosilicon is being acted on with the production of complex chlorinated silicon compounds, by the further chlorination of which the silicon tetrachloride is produced.

Once this initial stage is over, the formation of silicon tetrachloride takes place with great rapidity.

EXPERIMENTAL.

Preliminary Experiments.—Some preliminary experiments were carried out by placing 50 per cent. ferrosilicon in glass tubes and passing chlorine through them while the latter were heated to various temperatures in a Gattermann's bomb furnace.

At first a temperature of 300—310° was maintained. It was soon found, however, that glass tubes were quite unsuitable for use with ferrosilicon. In the first place, the ferric chloride produced by the chlorination of the iron sublimed down the tube, and soon caused it to block up, and the tubes usually broke when being cleaned out. Moreover, unless the stream of chlorine is very carefully regulated, the temperature of the reaction may rise so high that the glass may fuse at certain points.

The use of glass tubes, therefore, was abandoned in favour of ordinary iron gas-piping, 30 mm. bore, fitted at the end with ordinary corks. It was found that the iron piping was soon burnt through by the chlorine at that end of the tube where the chlorine entered and began to react with the ferrosilicon. The expedient of placing the ferrosilicon on movable iron troughs inside the tube was tried, but was abandoned, as the troughs stuck firmly to the inside of the tube (owing to the ferric chloride acting as a lute), and the latter could not be effectively cleaned out.

Although, when the temperature of the furnace was maintained at 300—310°, the iron tube was very rapidly attacked by the chlorine, it was found that by employing a lower temperature the corrosive action of the chlorine was very much diminished. A temperature of 180—200° was found to be very suitable. A temperature of 170° caused the action of the chlorine on the ferrosilicon to become so slow that it was abandoned in favour of the higher temperature. Moreover, by keeping the temperatures low, the yield of disilicon hexachloride (the substance it was desired to obtain in quantity) was practically doubled. Thus in the initial experiments, when the furnace was maintained at 300—310°, the yield of disilicon hexachloride in the crude silicon tetrachloride was about 4 per cent.

When the furnace was kept at 250—260° the yield of disilicon hexachloride rose to 4·6 per cent., whilst at 180—200° the yield rose to 8·6 per cent. At 170° the action of chlorine on ferrosilicon took place too slowly for effective work.

Apparatus for the Production of Silicon Tetrachloride and Disilicon Hexachloride in Quantity.

As the result of these preliminary experiments an apparatus for producing silicon tetrachloride in quantity was built up. In it chlorine from a cylinder was dried by passing through sulphuric acid, and then, by means of a T-piece, was led alternately through two iron tubes set in a Gattermann bomb furnace and charged with ferrosilicon. The ends of the tubes were fitted with ordinary corks through which glass leading-tubes passed.

The corks were best coated with paraffin-wax or bakelite varnish. A plug of glass-wool at the far end of the tubes arrested the ferric chloride, which slowly distilled down the tube, and tended to block up the leading tubes. The silicon tetrachloride was collected in a Winchester bottle.

This apparatus worked well for the production of a few kilos. of silicon tetrachloride and a few hundred grams of disilicon hexachloride. When, however, it became necessary to prepare about 50 kilos. of silicon tetrachloride, so that about 3 kilos. of disilicon hexachloride could be isolated therefrom, grave defects soon revealed itself in the apparatus.

In the first place the corks needed constant replacement and repair even when well coated with bakelite varnish. Moreover, they often become impregnated with disilicon hexachloride and the higher chlorides, which on contact with atmospheric moisture soon decomposed with the production of explosive silicon oxy-compounds. Consequently, the corks, after a time, became unpleasant to handle, since in forcing them into or withdrawing them from the tube explosions occurred, which, when much disilicon hexachloride had accumulated, could cause injury to the hands. It should be noted that all these compounds of silicon which contain silicon atoms directly united in the chain are, apparently, formed with the absorption of heat, and so are capable of explosion under suitable conditions.

Frequently in the course of the experiment the corks blew off without warning with considerable violence, either as the result of a sudden blockage in the tube by the sublimed ferric chloride, or possibly, on certain occasions, by the presence of excess of chlorine explosively causing the ignition of the higher chlorides formed in the tube (see p. 2859).

Leakage of chlorine from the corks could only be prevented with great difficulty, and as about 143 kilos. of chlorine were required for the production of the amount of silicon hexa- and tetra-chlorides needed, the leakage of chlorine became serious. It was, therefore, essential to devise chlorine-tight end-pieces, and after some experimenting, the corks were finally displaced by detachable iron caps screwed on to the ends of the tubes.

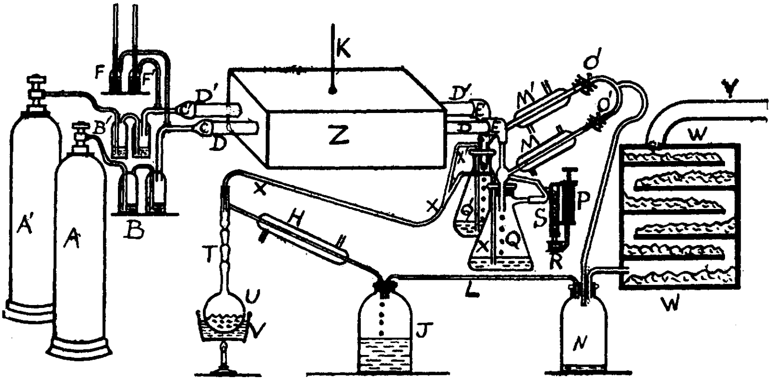
The threads were made gas-tight at first by the use of ordinary yellow soap (which acted admirably as a lute for chlorine), but later fine fibres of asbestos introduced into the threads were found to act better. The difficulty of chlorine leakage was thus surmounted, and the ends of the tube could be screwed off with ease and the tube withdrawn, washed out, and recharged when this was necessary.

Since blockages in the tubes invariably occurred after a certain interval of time, explosions could easily arise unless the pressure prevailing inside the tubes was properly controlled. This was done by attaching mercury manometers to the mouths of the tubes, any increase of pressure inside the tubes being indicated by the rise of mercury in these manometers, which also acted as safety valves.

Lastly, it was necessary to absorb chlorine and other corrosive vapours which passed through the apparatus. This was very efficiently done by means of a lime absorber. It consisted of a wooden box, 100 cm. long by 70 cm. wide, fitted with shelves so shaped that the chlorine passed over them in a zigzag fashion. The waste gases entered at the bottom, and escaped into the flues at the top through holes of about 3 cm. diameter bored in the shelves. The lime had to be changed every week, the face of the box being so arranged that the front opened like a door, so that the shelves could be cleaned out when necessary. The box was made chlorine-tight by luting with ordinary yellow soap. The complete apparatus is shown in Fig. 1. A and A^1 are two chlorine cylinders, each holding about 42·5 kilos. of liquid chlorine. B and B^1 are the two series of sulphuric acid wash-bottles, whilst D and D^1 are the two 3-cm. gas-pipe iron tubes, about 120 cm. long, fitted with iron leading pipes attached to iron screw-on caps, C and C^1. F and F^1 are the two mercury manometers attached by means of glass and rubber tubing to the leading tubes of D and D^1, so that the pressures prevailing inside the pipes D and D^1 are accurately known, an increase of pressure being indicated by the rise of mercury in F and F^1.

The mercury in the reservoirs of F and F^1 is covered with a layer of concentrated sulphuric acid, which protects the mercury to a large extent from vigorous attack by the chlorine gas. Z is a Gattermann bomb furnace, the internal temperature of which is indicated by the thermometer K. In these experiments the temperature was kept on the average between 180° and 200°. The tubes D and D^1 end in iron screw-on elbow joints E and E^1, from which a piece of iron pipe of 12 mm. bore projects into the two receiving vessels, Q and Q^1. These consisted of two 2-litre filter-flasks, in which almost all the crude silicon tetrachloride passing over from the apparatus condensed, only a very small amount passing away through the condensers M and M^1 and collecting in the bottle N.

FIG. 1.



An air-pump P provided with a mercury trap R and a drying tube S is directly united to the flasks Q and Q^1, and by forcing air into Q and Q^1 (after closing sundry clips controlling the exits from the flasks) the crude silicon tetrachloride could be forced up the tubes X and X^1 (which reach almost to the bottom of the filter-flasks Q and Q^1), along the pipe XX into the fractionating column T, and thus into the fractionating flask U, which is heated on a water-bath V.

The fractionating column employed was a Young's three-bulb evaporator still-head, which was fused on to a litre flask. The leading tube from the top of the distilling column T passes through a condenser H into a receiver J (a Winchester bottle). From J a leading tube L runs to the catch-bottle N, and thence a wide leading tube runs to the lime absorber WW. Here any chlorine and silicon tetrachloride vapours enter at the bottom, and after circulating over the lime on shelves in zigzag fashion, escape at the top into the flues. The absorption of chlorine and silicon tetrachloride by the apparatus was almost complete.

The iron piping was packed with coarsely crushed ferrosilicon, which commenced a few cm. in front of the place where the tubes enter the furnace, and extended for some 20 to 30 cm. down the tube, about 1 to 2 kilos. of ferrosilicon being used for each charge. This short length of ferrosilicon was found advantageous in that the chlorine was found to be completely absorbed by the short layers, and a longer length only tended to cause the tube to block up owing to the sublimed iron chloride condensing in the ferrosilicon at the far end of the tube. With short lengths of packing a considerable space was left in which the iron chloride could condense without choking the tube.

The method of working the apparatus was as follows: The tubes DD and D^1D^1 were charged with ferrosilicon, placed in the furnace, and their temperature was raised to 180—200°, the temperature being indicated by the thermometer K. Chlorine was then admitted in a moderately rapid stream, the rate being controlled by the screw valves attached to the cylinders A and A^1.

The action does not take place immediately. Usually the silicon tetrachloride begins to pass over in about thirty minutes after starting the operation. Occasionally, however, it was found that an hour's, two hours', and in some cases three hours' passage of the chlorine through the heated tube was necessary before the silicon tetrachloride began to pass over in quantity.

Temperature did not seem to play a great part in shortening the length of this preliminary period, as even when the furnace was maintained at as high a temperature as 300—310° the same phenomenon was observed, and keeping the temperature at 190—200° did not cause a sensible prolongation of this period of waiting before the silicon tetrachloride began to pass over. Also a very rapid initial stream of chlorine did not shorten sensibly the initial period.

This effect is, possibly, due to the fact that the chlorine must have time to attack the surface of the ferrosilicon and produce intermediate complex silicon chlorinated compounds before the production of silicon tetrachloride takes place. When, however, the action started it took place moderately rapidly with a considerable rise of temperature, and the silicon tetrachloride passed over in a steady stream and collected in the vessels Q and Q^1 as a yellow, fuming liquid.

The tubes are worked for about three hours at a time either simultaneously or alternately, but as a rule matters were so arranged that one tube was in full action whilst the other one was being pulled out and re-charged. The silicon tetrachloride condensed in the filter-flasks Q and Q^1, and was from time to time forced by the pressure of the chlorine from the cylinders up the pipes X and X^1 into the fractionating flask U. When this was done the screw clips were once more opened and the action continued. When, for any reason, it was inconvenient to use the pressure of the chlorine from the cylinders A and A^1 for forcing the liquid from Q into U, air-pressure applied by the air-pump P was used for this purpose.

The silicon tetrachloride collecting in U was then fractionally distilled, the distillate being collected in the Winchester bottle J. J when filled is removed and replaced by another Winchester bottle. The silicon tetrachloride is stored in these bottles, using ordinary corks well boiled in paraffin wax, the corks being taken out of the paraffin bath and while still warm being forced into the neck of the bottle, and covered over with a layer of melted paraffin, so as to prevent any danger of atmospheric moisture reaching the silicon tetrachloride. When sealed in this way the silicon tetrachloride can be stored for months without depreciation.

When the flask U became nearly full of residues of high boiling point, the water-bath was replaced by an oil-bath heated to a higher temperature.

The disilicon hexachloride passed over at 147—149°, and was collected separately and fractionated in a separate flask, also provided with a fused-on Young evaporator still-head. There was thus left behind in U a gradually increasing amount of residues of high boiling point, which were later proved to consist of higher chlorides of silicon (see below), besides a mass of tarry material and a black, solid residue, much like animal charcoal in appearance.

Method of Charging and Discharging the Tubes.—When it was observed that the supply of silicon tetrachloride dropping into *Q* or Q^1 from one of the tubes diminished, or when the pressure in the tube began to increase rapidly (as indicated by the manometers *F* or F^1), it was known that either the tube was becoming exhausted, or that it was becoming choked up by sublimed ferric chloride. This occurred, on the average, every three hours. Consequently, it became necessary at the end of this time to withdraw the tube, clean it out, recharge it with ferrosilicon, and replace it in the furnace.

To do this, the supply of chlorine is cut off from the tube, then the end caps *C* and *E* are rapidly unscrewed (these caps are cold enough to be touched by the hand, since they project nearly 30 cm. from the furnace), the tube is drawn out over iron rollers (not shown in the illustration), then, while hot, rapidly transferred to a sink, a cork fitted with a leading tube is attached to one end (after first withdrawing the plug of glass wool), and a supply of cold water allowed to flow into the tube. This water, entering the tube, is soon heated to boiling, and largely converted into steam, which blows the contents of the tube through the open end of the tube and effectively and rapidly cleans out the ferric chloride in the tube. The stream of cold water is allowed to flow through the tube until it runs clear, when the ferric chloride has been completely removed. The iron rod with a pointed end is then applied to clear out any particles of ferrosilicon still adhering to the tube, and the wet, clean tube is then transferred to a combustion furnace and dried by heating, while a current of air is blown through it. The tube is then removed from the combustion furnace, rapidly charged with 50 per cent. ferrosilicon, as described on page 2847, and replaced in the furnace (being run in over the iron rollers above-mentioned), the caps at *C* and *D* are screwed on, and the stream of chlorine is once more let into the apparatus.

As each iron tube corroded very rapidly just at one point, namely, at the end where the chlorine enters and acts on the ferrosilicon, in recharging care was taken to place the charge at the end of the tube opposite to that end previously used, so that the corrosion should take place equally at each end. However, even with this precaution, the average life of each iron tube was not more than six experiments, the chlorine burning a hole through the iron piping at the point where the action was most intense.

The 50 per cent. ferrosilicon washed out of the tube is well washed with water until free from iron chloride, dried in an air-oven, and once more was used for recharging a second tube. The ferrosilicon was thus used over and over again until consumed.

At the same time considerable wastage occurred, owing to particles of the ferrosilicon escaping as a suspension in the washing water.

Too finely powdered ferrosilicon was found not to be suitable for use, as blockages in the tube were thereby easily occasioned.

Since traces of higher chlorides accumulate at the ends of the tube and are converted by the washing water into explosive oxy-compounds, these, on striking with the iron rod or on scraping, may explode if in considerable amount, so that a certain amount of care must be taken not to allow these residues to accumulate to any great extent in the tubes.

This apparatus, which was gradually evolved out of repeated failures and mishaps, worked very smoothly and efficiently, and by means of it about 54 kilos. of silicon tetrachloride were prepared by the passage of 143 kilos. of chlorine gas over about 50 kilos. of 50 per cent. ferrosilicon.

From the crude silicon tetrachloride, which was distilled as fast as it was produced in the continuous fractionating apparatus, there were produced about 3 kilos. of disilicon hexachloride and about 500 grams of residues which contained nearly 200 grams of trisilicon octachloride.

Apparatus for Distilling the Crude Silicon Tetrachloride so as to Separate the Higher Chlorides.

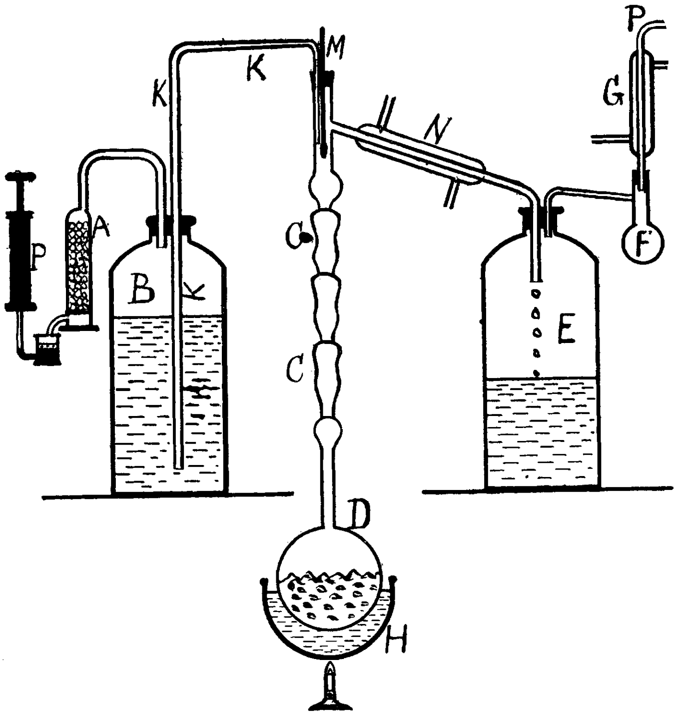
The problem of dealing with large quantities of the highly volatile silicon tetrachloride (b. p. 59°) is complicated by the fact that atmospheric moisture decomposes it, with the formation of hydrochloric acid and the deposition of silicic acid.

Consequently, all the vessels in which the liquid is kept must be most carefully dried before allowing the silicon tetrachloride to enter.

A description of the apparatus used for distilling and fractionating this silicon tetrachloride in the absence of atmospheric moisture may prove useful to other workers, as the final form was arrived at only after much troublesome experimenting. The apparatus finally used is shown in Fig. 2.

A is a vessel filled with coarsely granulated calcium chloride. To this vessel an air-pump, *P*, is attached, connexion being made through a mercury trap, *T*, to prevent the silicon tetrachloride vapours reaching the pump. By this means dry air can be forced into the Winchester bottle, *B*, containing the crude silicon tetrachloride to be distilled. As a result of this increased air-pressure, the crude silicon tetrachloride is forced up the tube *KK* into the fractionating flask *D*, which is fitted with a Young's three-bulb evaporator still-head, *C*, fused on to *D*. At the top of the still-head *C* is a thermometer, *M*. The leading tube from the still-head passes through a condenser, *N*, as shown. The flask *D* is placed on a water-bath, *H*, and after the proper amount of crude silicon tetrachloride has been forced into *D* from the reservoir *B*, it is fractionated, the residual disilicon hexachloride (b. p. 145°), together with the higher chlorides, remaining behind in *D*, whilst the volatile silicon tetrachloride (b. p. 59°) passes up the column *C* and, condensing in *N*, runs into the receiver *E*. *F* is a catch for any silicon tetrachloride vapour that does not condense in *E*, *G* being an auxiliary condenser. In hot weather *F* should be immersed in ice. *P* leads out to the flues.

Fig. 2.



The bottle *B*, the distilling column *C*, the bottle *E*, and the flask *F* are all fitted with corks which have been boiled in paraffin wax.

By means of this apparatus many kilos. of silicon tetrachloride can be continuously distilled free from contact with atmospheric moisture, and separated from the residues of high boiling point, which thus accumulate in the flask *D*.

As the liquid concentrates in *D* it becomes dark brown, almost black, whilst the liquid in *E* consists of almost pure silicon tetrachloride containing a little dissolved chlorine. It is of a yellowish colour, but can be rendered colourless by allowing it to remain for some days in contact with freshly-ignited animal charcoal, followed by redistillation.

When a sufficient quantity of residues has collected in *D*, the water-bath, *H*, is replaced by an oil-bath, and the residues are distilled, the bulk of the material passing over (after the silicon tetrachloride has been removed) at 147—148° under the ordinary atmospheric pressure. There remains in *D* some black fluid residues, and a black powder resembling animal charcoal.

Redistillation of the Crude Disilicon Hexachloride.

The crude disilicon hexachloride distilled, as above described, from the residues was now purified by keeping it over freshly ignited animal charcoal, and was then fractionally distilled from an apparatus made entirely of glass, the fractionating column employed being a Young's three-bulb evaporator still-head fused to the flask. During this operation the most rigorous precautions had to be taken to dry most thoroughly all the vessels used in the distillation, otherwise a turbid distillate would result.

Ordinary drying by washing out with alcohol followed by ether and blowing warm air through the apparatus was not efficient enough. The flasks had to be heated nearly to redness (after the preliminary washing with alcohol and ether), and then, after blowing out with hot air, must be attached still fairly hot to the receiver. The pure substance boils at 144—145·5°/760 mm. The boiling point, 145—146°, given by Gattermann and Weinlig (*loc. cit.*) is undoubtedly a little too high. The boiling points under diminished pressures were also determined as follows:

Boiling Points of Disilicon Hexachloride.

Pressure. mm.	B. p.	Pressure. mm.	B. p.	Pressure. mm.	B. p.
12	40°	41	61°	130	92°
12·5	43	50	65	135	93
13	46	53	66	140	94
14	47	90	80	150	95
17	48·5	95	81	181	98
19	49	105	84	195	101
20	50	110	86	200	102
22	53·5	119	89	222	103·5
27	56	122	90	760	144–145·5
31	60	126	91		

The pure substance froze to a white, ice-like mass at $-3°$, which did not finally melt until a temperature of $-1°$ was reached.

The density of disilicon hexachloride determined with 200·6684 grams was found to be D_4^{15} 1·5624. Troost and Hautefeuille gave 1·58 at 0°.

The refractive index for sodium light (*D* line) as determined by the hollow prism method was found to be 1·4748 at 18°. Another determination by a drop method gave 1·4775 at 14·5°. Gattermann and Weinlig gave the refractive index for "red light" as 1·45.

Although Gattermann and Weinlig showed (*loc. cit.*) that when water acts on disilicon hexachloride, silico-oxalic acid is produced, thus:

$$Si_2Cl_6 + 4H_2O = (SiO_2H)_2 + 6HCl,$$

in the form of a white precipitate, insoluble in acids, but soluble in alkalis with the evolution of hydrogen, yet it seems to have escaped their notice that soluble colloidal forms of silico-oxalic acid are produced at the same time. This was proved as follows: disilicon hexachloride was treated with a little water, when a white precipitate of silico-oxalic acid separated, which was collected. The residual clear liquid, however, still contained some silico-oxalic acid in colloidal solution, as was proved by adding to the liquid a few drops of concentrated ammonia solution, when a considerable gelatinous precipitate was obtained. This colloidal form of silico-oxalic acid is now being further investigated, and an account will be given in another paper.

Analysis of Disilicon Hexachloride.—By means of a small pipette made of a piece of small-bore glass tubing drawn out at one end and fitted with a rubber teat at the other end (the whole pipette being most carefully dried before use), 1·3029 grams of disilicon hexachloride were transferred to a dry weighing bottle, exactly weighed, and then decomposed by water rendered alkaline with ammonia. The contents of the weighing bottle were finally rinsed out, the precipitated silicic acids collected, the washings exactly neutralised with nitric acid and titrated with silver nitrate, using potassium chromate as indicator. (Found, Cl = 78·9. Calc., Cl = 78·9 per cent.)

Isolation and Properties of Trisilicon Octachloride, Si_3Cl_8.

After the crude disilicon hexachloride had been distilled over, there remained in the flask a dark-coloured mass, consisting of liquid and solid. The liquid was poured into a fractionating flask, and there remained a black, amorphous powder resembling animal charcoal, and weighing 160 grams. This powder is undergoing examination.

The black liquid, weighing about 377 grams, was now distilled, using a rod-and-disk fractionating column fused on to the flask, and heating on a metal bath.

After separating the disilicon hexachloride still in the liquid between 141° and 147° (atmospheric pressure), the temperature rose rapidly to 170°, and then more slowly to 185°. The weight of the fraction boiling at 141—185° was 128 grams.

The temperature then rose rapidly from 185° to 200°, when the receiver was again changed, 64 grams distilling between 185° and 200°. The bulk of the liquid, amounting to 185 grams, passed over, however, at 200—220°, a large portion of which distilled at about 215—217°.

There remained in the flask about 20 c.c. of a dark-coloured liquid boiling at above 220°, which was worked up separately (see below).

The distillates, which consisted of yellow, fuming liquids, were now subjected to careful fractionation under diminished pressure, using a 21 rod-and-disk fractionating column fused on to a glass flask, and heating from an oil-bath. The liquids were easily separated into some disilicon hexachloride and trisilicon octachloride, the latter being obtained pure after one or two fractionations. The amount of pure trisilicon octachloride was about 150 grams, about 30 grams of impure liquid being simultaneously isolated.

The published accounts of the boiling point of this substance vary considerably. Thus, Gattermann and Weinlig (*loc. cit.*) give 210—215°, whilst Besson and Fournier (*loc. cit.*) give 215—218°. There is no doubt, however, that Besson and Fournier's product was not pure. The boiling point of the above product was 210—213° under the atmospheric pressure, agreeing closely with Gattermann's value. The substance slowly decomposes when boiled under the ordinary pressure, giving rise to a dark-coloured residue. It is this partial decomposition of the trisilicon octachloride that is responsible for the fact that the boiling point is not very sharp under atmospheric pressure. When the liquid is distilled, however, under diminished pressure, no decomposition occurs; the liquid can be repeatedly distilled under diminished pressure to the last drop, without any discoloured residue appearing in the flask. The boiling points were determined as follows:

Pressure. mm.	B. p.
17	100°
22	106
24	110
30	113
47	124
53	126·5
60	129
65	133
69	134·5
72	135·5
74	137°
80	139
83	141
90	143
93	144
95	145
108	147
110	149
760	210–213

The density was found to be D^{15}_{4} 1·61, and the refractive index for sodium light (*D* line) 1·5135 at 14·5°. Gattermann and Weinlig (*loc. cit.*) gave the refractive index for "red light" as 1·52.

The liquid was analysed in the same way as disilicon hexachloride (p. 2853). (Found, Cl = 76·99. Calc., Cl = 76·97 per cent.)

Isolation of Higher Chlorides.

After separating the trisilicon octachloride as above described there remained in the flask about 20 c.c. of a black liquid which boiled at above 220°. This was now subjected to fractional distillation under diminished pressure in a specially constructed small glass flask, fitted with a rod-and-disk fractionating column, the flask and fractionating column being fused together.

After very considerable difficulties, founded principally on the fact that the silicon chlorides must not be exposed to moist air, and the fact that only very small quantities were distilled, at least three distinct substances were separated after repeated distillation: (1) a viscous, colourless liquid (3 grams), boiling at about 150°/15 mm.; (2) a viscous, colourless liquid (2 grams), boiling at about 190°/15 mm.; and (3) a white, crystalline solid (0·5 gram), which melted at about 218°, and distilled at about 210°/12 mm. It was soluble in dry benzene or light petroleum, and could be crystallised therefrom. The examination of these substances is being continued.

These chlorides, when thrown into water, yield white, amorphous products, easily combustible, which are no doubt the higher analogues of silico-oxalic and mesoxalic acid. These white substances also dissolve in potassium hydroxide to a clear solution with the evolution of hydrogen.

The examination of these products is being continued.

There remained in the flask at least 13 grams of a black, viscous mass, like tar or pitch, which was soluble in ether, insoluble in absolute alcohol, and evolved hydrogen with sodium hydroxide. The latter product, however, is still undergoing examination.

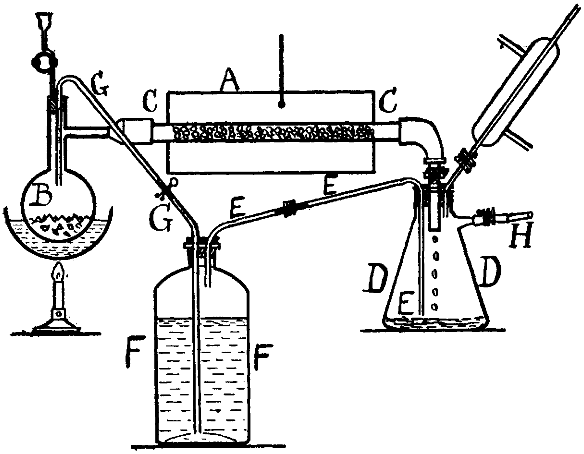
Distillation of Silicon Tetrachloride over Silicon.

According to Gattermann and Weinlig (*loc. cit.*), silicon and silicon tetrachloride interact as follows:

$$3SiCl_4 + Si = 2Si_2Cl_6.$$

In order to test this the following apparatus was employed:

FIG. 3.



By means of air pressure (from an air-pump) applied to the Winchester bottle *F*, pure silicon tetrachloride contained therein could be forced into the weighed flask *B*, which is heated on the water-bath. This silicon tetrachloride was then distilled from the flask *B* through an iron pipe *C* packed with commercial silicon broken into a coarse powder and heated in a Gattermann's bomb furnace *A*. The iron tube was about 120 cm. long and 3·1 cm. in internal diameter, with screwed-on iron terminal caps and connecting pieces, the screw-threads being made gas-tight by asbestos packing. The silicon tetrachloride passing through the tube *C* is condensed in the two-litre filter flask *D*. By means of an air-pump attached to *H* the silicon tetrachloride accumulated in *D* could (after closing certain clips connected with the exit tubes from the apparatus) be forced back up the tube *EEE* into the reservoir *F*, and thence, if required, up the tube *GG* back into the flask *B*, so that the silicon tetrachloride in *F* could be repeatedly distilled over the silicon in *CC* as many times as desired.

By means of this apparatus 3 kilos. of silicon tetrachloride free from disilicon hexachloride were repeatedly distilled over silicon in the tube *C*, first of all when the latter was maintained at 200°, then at 280°, then at 310°, and lastly at 340°.

However, in no case were noticeable amounts of disilicon hexachloride found to have been formed in the distilled silicon tetrachloride.

Hence it is proved that the 20 per cent. yield of disilicon hexachloride stated by Gattermann and Weinlig to have been produced by the action of chlorine on silicon at 300—310° could not possibly have arisen, as they supposed, from the action of silicon tetrachloride on silicon.

Distillation of Silicon Tetrachloride over Ferrosilicon.

The preceding experiment was repeated, the silicon in the tube being now replaced by 50 per cent. ferrosilicon. However, in this case, also, no noticeable amounts of disilicon hexachloride could be proved to be produced when 3 kilos. of silicon tetrachloride were distilled over the mass, even when the tubes were heated to 300° and 340°.

It was thought that although ordinary silicon tetrachloride when distilled over ferrosilicon will not give rise to disilicon hexachloride, nevertheless it might be possible that silicon tetrachloride at its moment of formation might react with ferrosilicon to produce some disilicon hexachloride.

The easiest way to test this was to pass chlorine over a very long length of ferrosilicon, so that the silicon tetrachloride produced in the first part of the tube would then react with more ferrosilicon as it passed in the vaporous condition down the tube. Consequently, the following experiment was carried out:

A piece of Jena combustion tube, about 200 cm. long and 2 cm. bore, was drawn out at one end and bent at right angles. It was filled with a long layer of 50 per cent. ferrosilicon in the form of a coarse powder, and the tube was placed through two bomb furnaces in succession, and was therein heated to 300—310°, while a slow current of dry chlorine was passed through the tube. The resulting silicon tetrachloride was received in a distilling flask immersed in cold water.

It was found that when the action commenced, the chlorine was practically completely absorbed by the first 15 or 17 cm. of heated ferrosilicon, so that the silicon tetrachloride would have every opportunity as it passed over the succeeding lengths of ferrosilicon to react with more silicon to produce disilicon hexachloride. However, the resulting silicon tetrachloride was found on distillation to contain less than 4 per cent. of disilicon hexachloride. Since the average yield of disilicon hexachloride produced by passing chlorine over short lengths of ferrosilicon considerably exceeds this, it is quite certain that the effect of passing silicon tetrachloride over a long length of heated ferrosilicon is not to increase the yield of disilicon hexachloride. If anything, it led to a diminution of the yield.

These experiments prove conclusively that the Gattermann-Weinlig reaction certainly does not proceed to a noticeable extent at low temperatures, and that therefore their explanation of the presence of disilicon hexachloride and higher chlorides in the silicon tetrachloride produced by chlorinating silicon or ferrosilicon is inadmissible.

Action of Chlorine on Disilicon Hexachloride.

The author's theory that complicated chlorinated silicon compounds are first produced when chlorine acts on silicon or metallic silicides, and that silicon tetrachloride is formed from these by the further action of chlorine, was now put to the test of experiment, and it was definitely poved that chlorine acts vigorously on disilicon tetrachloride (and no doubt still more vigorously on the more unstable higher chlorides) at 300—340° so as to break up the chain of directly united silicon atoms, with the production of silicon tetrachloride, thus:

$$Cl_3Si\cdot SiCl_3 + Cl_2 = 2SiCl_4.$$

It was proved that disilicon hexachloride burns directly to silicon tetrachloride in the presence of chlorine, the experiment being carried out as follows:

A stream of chlorine (dried by passing through concentrated sulphuric acid) was passed into a 150 c.c. flask containing about 50 grams of pure disilicon hexachloride and heated on an oil-bath, the temperature of which was gradually raised to 165° or 166°. The leading tube of the distilling flask was inserted firmly through a cork at one end of an iron tube, whilst at the other end of the iron tube there was an iron elbow joint screwed on, which was fitted with a reducer. A piece of iron piping from this projected into a receiving flask, passing in through a rubber stopper. The receiving flask had its leading tube projecting into a similar flask, the two latter flasks being immersed in ice.

The iron tube was contained in a Gattermann's bomb furnace, the temperature of which was maintained at about 340°.

A continuous stream of chlorine was now passed through the apparatus. So long as the temperature of the oil-bath in which the first flask was immersed was not sufficiently high to cause the disilicon hexachloride to boil, the silicon tetrachloride was not noticed to be passing over rapidly into the receiving flask. Also, if the iron tube was kept at about 120—130° and the disilicon hexachloride was allowed to distil through it in a stream of chlorine, no inflammation followed. If, however, the temperature of the tube was kept at 300—340°, as soon as the vapour from the boiling disilicon hexachloride, mixed with chlorine, reached the iron tube a mild explosion took place, a red flame shot back into the flask, and the disilicon hexachloride could be observed burning with a reddish flame all over its surface in the atmosphere of chlorine.

When the supply of chlorine was checked the flame rose and burnt round the end of the tube projecting into the flask through which the chlorine entered, the chlorine here burning in an atmosphere of disilicon hexachloride vapour. Dense, brown fumes accompanied the combustion of the disilicon hexachloride, and at the same time the silicon tetrachloride produced as the result of the combustion streamed through the iron tube, and rapidly collected in the receiving flask, the liquid being of a dark colour.

The experiment, however, must be carried out with caution, or it may become dangerous. Although on one occasion about 45 grams of pure disilicon hexachloride were burnt to silicon tetrachloride in this manner with only a mild initial explosion, yet in another experiment a violent explosion suddenly occurred towards the end of the operation, the first flask being hurled with great violence into the air and shattered with a loud report.

The liquid which distilled over was proved to be almost entirely silicon tetrachloride, distilling almost to the last drop between 50° and 70°, and leaving an inappreciable weight of a brown film in the flask. Disilicon hexachloride boils at 145°, whereas silicon tetrachloride boils at 59°.

Although disilicon hexachloride will thus catch fire and burn in a stream of chlorine to silicon tetrachloride, yet it was proved that this action only took place at temperatures higher than the boiling point of the hexachloride. At the ordinary temperature disilicon hexachloride does not combine with chlorine to a noticeable extent.

This was proved as follows: Dry chlorine from a cylinder was passed first through a wash-bottle containing concentrated sulphuric acid, and then into a distilling flask containing about 270 grams of pure disilicon hexachloride, the chlorine escaping through another wash-bottle also containing concentrated sulphuric acid.

A very considerable amount of chlorine was observed to dissolve in the disilicon hexachloride in the flask, without, however, any visible signs of a chemical action taking place; thus no sensible evolution of heat could be detected as the chlorine entered the flask. The stream of chlorine was passed through the disilicon hexachloride for about four hours, and the liquid containing the dissolved chlorine was then allowed to remain for twenty-four hours.

When the liquid in the flask was heated (being connected for this purpose with a condenser and a receiver rendered moisture-proof by calcium chloride tubes), on the first application of heat the disilicon hexachloride appeared to boil at quite a low temperature. This effect, however, was entirely due to the escape of the dissolved chlorine, and on distilling the 270 grams of disilicon hexachloride certainly less than 1 c.c. of liquid passed over below 100°, thus conclusively proving that no appreciable amount of silicon tetrachloride (b. p. 59°) was produced by the prolonged action of chlorine on disilicon hexachloride.

This experiment also proved the very great solubility of chlorine in disilicon hexachloride, a fact which does not appear to have been noted before.

The refractive indices of disilicon hexachloride and trisilicon octachloride were kindly determined for the author by Mr. H. R. Nettleton.

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