

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]
**A REVISION OF THE ATOMIC WEIGHT OF SILICON. THE
RATIO $\text{SiCl}_4:\text{SiO}_2$ ¹**

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F. W. Clarke, in the fourth edition of his "Recalculation of Atomic Weights,"² gives a summary of the work on the atomic weight of silicon up to that time. Since the publication of Clarke's memoir, however, great advances have been made in the methods of purifying and handling silicon tetrachloride.

The first and, up to the present time, the most exhaustive study of the atomic weight of silicon, using the method of distillation in an all-glass vacuum apparatus, is that carried out by Baxter and his co-workers.^{3,4} A determination of the ratios $\text{SiCl}_4:\text{Ag}$ and $\text{SiBr}_4:\text{Ag}$ gave, in the final series with each compound, respectively, $\text{Si} = 28.067$ and $\text{Si} = 28.059$, or an average value 28.063, on which the accepted value of 28.06 is based.

Hönigschmid and Steinheil,⁵ using SiCl_4 which had been very carefully purified by A. Stock, by a method which has been described in connection with the purification of other compounds of this type,⁶ determined the ratio $\text{SiCl}_4:\text{Ag}$. As the result of four very concordant values, they found $\text{Si} = 28.105$. An investigation of the purity of their silicon tetrachloride by the measurement of its vapor pressure at 0° showed that no change was taking place after four distillations.

By a novel method of determining the ratio $\text{SiCl}_4:\text{H}_2$, Stock and Kuss⁷ found $\text{Si} = 28.15$. From the nature of this investigation the value obtained cannot be given the weight which is due the researches of Baxter and of Hönigschmid.

In the present work silicon tetrachloride was purified by repeated distillation in a vacuum, using fractionating columns filled with glass pearls. The pure material was taken off in sample bulbs of fused quartz, the bulbs broken in a platinum crucible under a partially frozen solution of pure hydrochloric acid, and the resulting silica gel dehydrated and weighed.

This ratio has been used before, most recently by Becker and Meyer,⁸ but at that time the method of purification by repeated distillation in a

¹ From a dissertation submitted by Perry S. Brundage to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Clarke, Third Memoir, *Nat. Acad. Sci.*, **16**, 222 (1920).

³ Baxter, Weatherill and Scripture, *Proc. Am. Acad. Arts Sci.*, **58**, 245 (1923).

⁴ Baxter, Weatherill and Holmes, *THIS JOURNAL*, **42**, 1194 (1920).

⁵ Hönigschmid and Steinheil, *Z. anorg. allgem. Chem.*, **141**, 101 (1924).

⁶ Stock and Kuss, *Ber.*, **56B**, 1463 (1923).

⁷ Stock and Kuss, *ibid.*, **56B**, 314 (1923).

⁸ Becker and Meyer, *Z. anorg. Chem.*, **43**, 251 (1905).

vacuum had not been developed, and the method of taking off samples for analysis allowed more chance for error.

The Purification of Silicon Tetrachloride

With minor changes, the procedure followed that developed by Baxter and his co-workers,³ Silicon tetrachloride, obtained from the General Electric Company, was repeatedly distilled in a vacuum, using fractionating columns containing glass pearls. A modification of the glass valve was adopted because it was felt that with the type used by Baxter (Fig. 1, A) there was danger of breaking the tube at *a*. The first type tried was that used by Hönigschmid and Chan⁹ (Fig. 1, B). This, however, gave a cloud of extremely fine glass fragments which were carried throughout the apparatus when the thin-walled bulb at *b* (Fig. 1, B) was broken, so this was discarded in favor of the valve shown in Fig. 1, C. Here the hammer, *d*, weighted with mercury, breaks the spiral capillary *c*. In this type there seems to be little danger of breaking the apparatus and no fine fragments of glass are formed. The operation of this valve was very satisfactory.

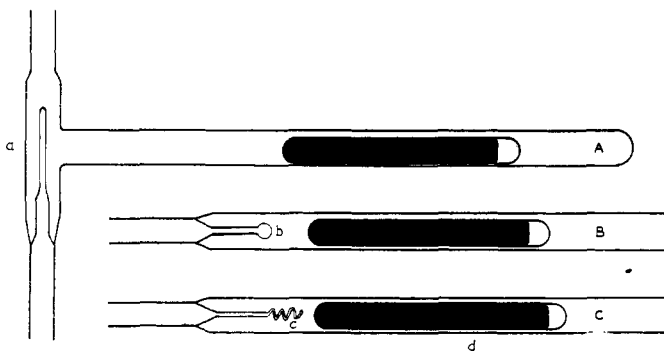


Fig. 1.

In pumping out the apparatus a mercury diffusion pump, backed by a rotary oil pump, was used. In all cases the apparatus was allowed to stand at least overnight, and readings on the McLeod gage were taken to be sure there was no leak. Phosphorus pentoxide was used as a drying agent in the McLeod gage.

After the start, where liquid air and carbon dioxide snow were necessary to remove the more volatile materials present, the distillation was carried out by cooling the receiver with an ice-salt mixture, the distillation flask being kept at room temperature. The distillation column was surrounded by a jacket which was kept cool by ice, so that there was a constant reflux of material over the glass pearls. In every distillation a small heavy fraction was left in the distillation flask and before sealing off this flask, the receiver was gently warmed, the distillation flask cooled and a small light fraction distilled back into it. In this way both a light and heavy fraction were removed at each distillation.

The best evidence for the purity of the material is the constancy of the value obtained from samples taken at rather widely separated points in the course of the distillations.

The number in the "Fraction of SiCl_4 " column in Table I shows the number of distillations which were made before the material destined for analysis was taken off from the main line of distillation.

⁹ Hönigschmid and Chan, *Z. anorg. allgem. Chem.*, **163**, 326 (1927).

Purification of Other Materials

Water.—Water from the laboratory still was twice redistilled, once from alkaline permanganate (which had been allowed to stand for some time) and once from very dilute sulfuric acid. The condensers were constructed of block tin tubes fitted to Pyrex flasks with constricted necks, which served as stills. The connections were made by a water seal, no cork or rubber being used. The water was distilled directly into the platinum crucible just before hydrolysis was started.

Hydrochloric Acid.—The best c. p. acid was diluted with an equal volume of pure water and distilled from a Pyrex flask through a quartz condenser, fitted to the constricted neck of the flask by a liquid seal. No cork or rubber or other material was used. The first and last thirds of the acid were discarded. The pure acid was distilled directly into the platinum crucible just before hydrolysis was started.

Phosphorus Pentoxide.—The ordinary c. p. material was sublimed in a current of pure oxygen in the usual way.

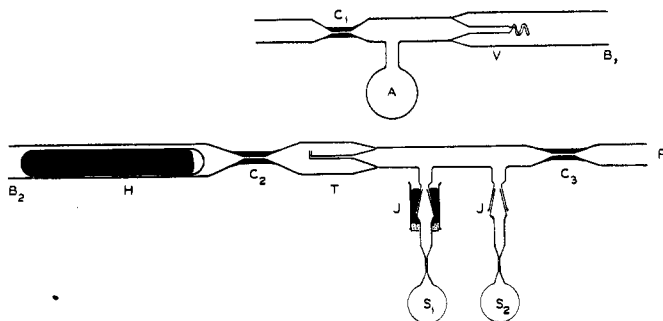


Fig. 2.

Method of Taking Samples for Analysis.—The apparatus used in taking samples for analysis is shown in Fig. 2. A large sampling bulb A with a valve V was sealed into the main distillation train, and after filling was sealed off at C_1 . B_1 and B_2 were now sealed together and the whole system evacuated through P and sealed off at C_3 . The valve V was then opened by allowing the hammer H to break the spiral capillary. The trap T was used to prevent any fragment of glass going into the sample bulbs S_1 and S_2 .

One of the mercury seals used around the joints connecting the sampling bulbs to the rest of the apparatus is shown on S_1 . The glass tube is held in place by a small cork so that the whole is easily removed.

The fused quartz sample bulbs S_1 and S_2 were then filled by cooling, and the slender capillaries sealed off with a very fine gas-oxygen flame.

The weight of the whole bulb and joint system was found before connecting it to the apparatus. After the bulb was sealed off from the joint, the weight of the joint was found, and thus the weight of quartz in the bulb itself. Subtracting this from the weight of the whole sealed sample gave the weight of SiCl_4 .

After sealing off the samples and before opening the joints, bulb A was cooled in liquid air to remove all traces of silicon tetrachloride and capillary

C₂ sealed off. This prevented any possible deposition of silica on the joints, which were, however, momentarily dipped in sodium hydroxide, and then rinsed in acid to remove any trace that might have been left.

It is well known that quartz volatilizes rapidly on fusion. Experiments showed that it was necessary to keep the capillaries on the sampling bulbs very fine so that the loss of silica during the sealing off was not more than 0.01 or 0.02 mg. Experiments also showed that the joints could be cleaned completely from silica (from the silicon tetrachloride) and mercury, and that no appreciable amount of quartz was ground off from the joints during their use.

Weighings.—All weighings were made on a No. 10 Troemner balance with weights standardized to 0.01 mg. All weights were corrected to vacuum, the density of the air at the time of weighing being determined by readings of the barometer and the temperature and relative humidity in the balance case. For relative humidity measurements in the balance case, a hair hygrometer was used. This was checked frequently against a whirling psychrometer.

The density of dry air was plotted against pressure for a series of temperatures. The corrected barometric reading was modified by subtracting $0.38 \times v. p. H_2O \times (H/100)$, where H is the relative humidity. This gave the pressure at which dry air would have the same density as the moist air at barometric pressure and relative humidity H . The graph was then entered on the proper isotherm, and from the pressure the density was determined. We have used other methods, such as weighing a standardized sealed bulb, but prefer the method outlined. It has the advantage that the readings are taken at the time of weighing rather than before or after, and seems to us easier.

The density of the weights was assumed to be 8.4; the density of fused quartz and of the silica formed by hydrolysis, 2.20. The densities of the sealed samples were determined separately for each sample by weighing in air and under distilled water in the usual way. All weighings were made by the method of substitution, except that in the standardization of weights the method of transposition was considered more convenient and so used. In weighing the platinum crucible in which hydrolysis was carried out, a similar platinum crucible weighing within 0.2 g. was used as a tare, and carried through the same heating treatment as the one in which hydrolysis occurred.

Analysis

Pure water and hydrochloric acid were distilled into a rather large platinum crucible and the quartz bulb with the sample of silicon tetrachloride put in this solution, which contained about 6 per cent. hydrochloric acid. The solution was then partially frozen by carbon dioxide snow, so that the bulb was held firmly to the bottom of the crucible. The bulb was

then broken under the liquid by tapping with a stiff platinum wire (which was left in the crucible).

The crucible and its contents, with the carbon dioxide snow, were transferred to a large casserole containing several pieces of cracked ice. The whole was carefully covered and allowed to stand overnight to allow the hydrolysis to proceed slowly as the temperature rose. The following morning the crucible contained a clear, smooth silica gel.

This gel was then slowly dehydrated, for several hours, in an air-bath, at 90 to 95°. After this treatment, which usually lasted overnight, the contents of the crucible had become a dry white flaky mass.

The crucible was then placed on a platinum disk in an electrically heated crucible furnace and ignited to constant weight.

Another similar furnace was connected in series and used to give the tare crucible the same ignition treatment.

The temperature was raised rather gradually, the usual times being one hour at 400°, one hour at 600°, two hours at 850°, two hours at 950° and finally at about 1080° until the weight became constant. Experiments showed that once a constant weight under this treatment was reached, further heating, even into the 1100° range, caused no further loss in weight.

Previous investigators used pure water, partially frozen, for this hydrolysis. In our preliminary experiments, however, we were unable to make the reaction take place so slowly that there was no appearance of spattering. While no material may be lost in such spattering, it seemed safer to use the hydrochloric acid solution where hydrolysis was much slower and no sign of spattering was visible.

The final heatings were carried out in a crucible furnace with a platinum winding. The Chromel A windings at first used gave out rapidly at the high temperatures used and caused much trouble, but once the platinum windings were put on, the furnaces worked perfectly.

The silica prepared in this way was uniformly white and flaky, and there was no evidence of adsorption during weighings. Apparently after prolonged treatment at the high temperature it is quite inactive. The purity of material so prepared has been the subject of investigations by Meyer,¹⁰ who found no evidence of impurities present.

It was at first hoped that Pyrex bulbs would be satisfactory for the samples, but difficulties were found in their use. It was found that the heating necessary for dehydrating the silica gels caused a small loss in weight of the Pyrex glass from the bulb. This might have been corrected for partially by carrying an equal weight of Pyrex glass through the same treatment in the tare crucible, but a much greater trouble was found. During the dehydration at higher temperatures, reaction apparently takes place between the Pyrex and the contents of the crucible, and small spheres

¹⁰ Meyer, *Z. anorg. Chem.*, **47**, 45 (1905).

of material are formed instead of the flaky solid given when quartz bulbs were used. The extent of this reaction was dependent upon the time rate of temperature change, and by a very gradual dehydration could be largely eliminated. Results computed for those analyses where such a reaction had taken place, gave markedly low values for the atomic weight of silicon, indicating a loss of some material. Since the analyses would always be open to question if Pyrex glass were used, it was necessary to make our sampling bulbs of fused quartz.

Results

The results of all analyses where sampling bulbs of fused quartz were used are given in Table I. With the exception of one sample which was lost during hydrolysis, every analysis that was started was carried to completion, and is recorded in the table. The atomic weight of chlorine is taken as 35.457.¹¹

While the average rounds off to 28.103 in either case, we believe that those three analyses which are starred in the table should be given less weight than the others for the following reasons. Analyses 1 and 2 were the first ones run using fused quartz sampling bulbs, and these bulbs were so heavy that it was necessary to treat them very roughly in order to break them. This experience led to thinner bulbs for the remaining samples, and no further difficulty was encountered in breaking the remaining sample bulbs. Analysis 8 was in progress at a time when a great deal of difficulty was experienced with the furnace windings and the dehydration of the silica gel from this sample was twice interrupted for several days, so that it was subjected to much more handling than the others.

TABLE I
(Cl = 35.457)

Analysis	SiCl ₄ vac. wt. g.	SiO ₂ vac. wt. g.	Ratio SiO ₂ :SiCl ₄	Atomic weight Si	Fraction of SiCl ₄
1	2.11017	0.74587	0.353464	28.044*	XIII
2	2.53146	0.89563	.353800	28.132*	XIII
3	4.59854	1.62648	.353695	28.104	XV
4	2.86802	1.01447	.353718	28.110	XV
5	3.01710	1.06731	.353754	28.120	XV
6	2.90424	1.02706	.353642	28.090	XVII
7	2.55431	0.90357	.353743	28.117	XVII
8	2.80323	0.99175	.353788	28.129*	XVII
9	2.92542	1.03462	.353665	28.096	XVII
10	3.38901	1.19857	.353664	28.096	XVIII
11	2.10540	0.74458	.353653	28.093	XVIII
Average, including all analyses.....				28.103	
Average, omitting analyses 1, 2 and 8.....				28.103 ± 0.0027	

¹¹ "First Report of the Committee on Atomic Weights of the International Union of Chemistry," THIS JOURNAL, 53, 1627 (1931).

In the remaining 8 analyses everything ran smoothly and there is no reason for preferring one analysis to any other.

Discarding those three analyses which were known to be subject to more possibility of error than the others, and which are recorded only for the sake of completeness, we have a value, based on 8 analyses, of $\text{Si} = 28.103 \pm 0.0027$.

This is higher than the value 28.063 which Baxter³ obtained from the ratios $\text{SiCl}_4:\text{Ag}$ and $\text{SiBr}_4:\text{Ag}$. It is in excellent agreement with the value obtained by Hönigschmid and Steinheil,⁵ $\text{Si} = 28.105$, from the ratio $\text{SiCl}_4:\text{Ag}$. It is difficult to explain this deviation, which is almost certainly much greater than the experimental error involved in either of the analytical methods. Each of the two rounded-off values, 28.06 and 28.10, has strong evidence in its support, since in each case different compounds have been used and have given results in good agreement. More experimental work obviously is needed.

Some previous atomic weight work has been criticized¹² because the exact terrestrial source of the material used was not known. It is interesting to note, therefore, that in accord with all other work on non-radioactive elements, investigations¹³ have shown that silicon, regardless of its source, always has the same atomic weight and therefore the same isotopic composition.

Summary

Silicon tetrachloride, carefully purified by repeated distillation through efficient fractionating columns, in a vacuum in an all glass apparatus was hydrolyzed with a pure hydrochloric acid solution, and the ratio $\text{SiO}_2:\text{SiCl}_4$ determined. The mean of eight analyses gave the value $\text{Si} = 28.103 \pm 0.0027$.

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¹² "Annual Reports of the Progress of Chemistry," The Chemical Society of London, 1924, Vol. XXI, p. 30.

¹³ Jaeger and Dijkstra, *Z. anorg. allgem. Chem.*, **143**, 233 (1925); *Z. Electrochem.*, **32**, 328 (1926); Briscoe and Robinson, *Nature*, **117**, 377 (1926); Robinson and Smith, *J. Chem. Soc.*, 1262 (1926).