CLXIV.—*A Comparison of the Atomic Weights of Silicon from Different Sources.*

By Percy Lucock Robinson and Harold Cecil Smith.

RESULTS obtained in a recent redetermination of the atomic weight of boron (Briscoe and Robinson, J., 1925, **127**, 696) indicated that the value varies slightly with the source of supply. The values

10·818, 10·825, and 10·841 found for Asiatic, Tuscan, and Californian material respectively were tentatively explained as due to variation in the isotope ratio. This paper reviewed the evidence and stated the conclusion that, despite excellent work supporting the opposite contention, there was no inherent improbability in this suggestion. It is to be deplored that much of the earlier work on atomic weights has been on material of unspecified origin, as this makes the discrepancies valueless for statistical investigation. The necessity for further work on boron being obvious, the problem was attacked by comparing the densities of boric oxide from these and other sources. The results of this investigation supported the original conclusion (Briscoe, Robinson, and Stephenson, this vol., p. 70).

Late in 1924, Jaeger and Dijkstra (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 290; *Z. anorg. Chem.*, 1925, **143**, 233) showed that the densities of tetraethylsilicane indicated no difference in the atomic weight of silicon exceeding 0·019 unit, which corresponds to a density difference of 0·00010 unit—a remarkable degree of accuracy for the pyknometer method employed. The inconclusive character of these results (see Briscoe and Robinson, *Nature*, 1926, **117**, 377) led us to proceed with the redetermination of the atomic weight of silicon projected early in 1924 for the reasons given below.

A brief comparison of the geological occurrence of boron and silicon is appropriate here. Boron is widely distributed and forms about 0·001% of the earth's crust (Clarke and Washington, *Proc. Nat. Acad. Sci.*, 1922, **8**, 108). It is found primarily in tourmaline and datolite, from which it is liberated and subsequently concentrated, principally as calcium salts, by the drying up of lakes as in the Asiatic and American deposits, or artificially separated from the steam of fumaroles as at Volterra. Clearly, in each case the boron has been associated for a considerable period with the area in which it is found. Silicon, next to oxygen the most abundant element, occurs terrestrially to the extent of 25·80% (Clarke, "Data of Geochemistry," 1920, 30). The transportation of siliceous material is almost entirely by mechanical means and then only over short distances, which makes it probable that silicon has remained associated with the continental mass on which it is found for considerable geological periods. This would appear to be the case even if Wegener's displacement theory should eventually be substantiated. Thus boron and silicon, for different reasons, have probably retained for great periods of time their general relationship to that area of the earth's surface on which they are found.

Silicon presents certain well-known general chemical similarities

to boron, and, occurring as it does in three isotopic forms, Si = 28, 29, 30 (Aston, *Phil. Mag.*, 1920, **40**, 628 : Si = 30; confirmed, *Nature*, 1924, **114**, 273), appears to be a suitable element for the further investigation of the constancy of atomic weight.

Determinations of the atomic weight of silicon previous to 1920, fully discussed by Clarke (*Mem. Nat. Acad. Sci.*, 1920, **16**, 22), are tabulated below (Table I) together with more recent work, under the three heads : halide : silver ratio, halide : oxide ratio, and vapour density.

TABLE I.

Halide : Silver Ratios.

Pelouze, *Compt. rend.*, 1845, **20**, 1047	28·370
Dumas, *Annalen*, 1860, **113**, 31	28·077
Schiel, *ibid.*, 1861, **120**, 94	27·945
Baxter, Weatherill, and Holmes (preliminary paper), *J. Amer. Chem. Soc.*, 1920, **42**, 1194	28·111
Baxter, Weatherill, and Scripture, *Proc. Amer. Acad. Arts Sci.*, 1923, **58**, 245	28·063, 28·061
Hönigschmid and Steinheil, *Z. anorg. Chem.*, 1924, **141**, 101...	28·105

Halide : Oxide Ratios.

Thorpe and Young, J., 1877, **51**, 576	28·381
Becker and Meyer, *Z. anorg. Chem.*, 1905, **43**, 251	28·231
Meyer, *ibid.*, 1905, **46**, 45..	28·231

Vapour Density.

Jaquerod and Tourpaian, *J. Chim. phys.*, 1913, **11**, 269	28·496
Germann and Booth, *ibid.*, 1917, **21**, 81	28·306

The only values in this table which merit serious consideration from the point of view of high accuracy, as distinct from mere novelty of method, are the more recent halide : silver results. The hope that the comparatively simple and direct halide : oxide ratio might produce results of high accuracy is evidently not realised, probably on account of the difficulty of dehydrating the oxide. Reinvestigation of the method with the facilities now available might more nearly fulfil anticipations. The vapour density determinations are open to criticism on the lines suggested by Clarke (*loc. cit.*). The halide : silver ratios exhibit considerable variation, 27·945—28·370, although the four more recent values are in agreement to 1 part in 560 parts. They lie—though probably by that chemist's happy accident—on either side of Dumas's figure. There is a considerable discrepancy between Baxter's (*loc. cit.*) 1920 preliminary and 1923 final figures, *viz.*, 1 part in 550 parts. The International Committee (*J. Amer. Chem. Soc.*, 1925, **47**, 597) have given 28·06 as the rounded mean in spite of Hönigschmid's (*loc. cit.*) 28·105. Clearly, further investigation is required if the atomic

weight of silicon is to be known to a greater accuracy than about 1 part in 700 parts.

Outline of the Present Investigation.

With the element silicon the choice of a suitable compound for equivalent determination is limited to the halides, and of these the tetrachloride is certainly the most convenient. The silicates are indefinite in composition; the organic compounds, while occasionally of suitable stability and constancy of composition, are difficult to analyse with the required precision; and the oxide, into which a number of compounds may readily be converted, presents difficulties which have already been commented upon. Furthermore, the tetrachloride readily lends itself to a comparison of the atomic weights of material from different sources, provided a suitable method can be devised for the determination of its density with sufficient accuracy.

Silicon tetrachloride was prepared by chlorinating ferrosilicon, manufactured from silica, in one case from an unknown source, and in four others from known localities in Canada, the United States of America, Sweden, and France. As no British ferrosilicon of known origin was available, silicon was prepared from a Scottish pegmatite, and this was chlorinated. The sample of unknown origin was used in a purely preliminary manner to establish methods employed in the preparation, handling, and purification of the compound. About equal amounts of the five samples of known origin were prepared and they were individually subjected to a rigorous, but strictly uniform, process of purification. When pure, the density of each was determined by the use of glass floats calibrated as to density with extreme accuracy. The constancy of the molecular volume of the chlorides of the various isotopes being assumed, the apparent atomic weights were thus compared.

The Preparation of Silicon Tetrachloride.

Sources of Material.—Of the methods available for preparing silicon tetrachloride, the most convenient for producing it in quantity without using elementary silicon is that involving the chlorination of ferrosilicon, originally described by Warren (*Chem. News*, 1892, **66**, 112). Inquiries were therefore instituted into the production of ferrosilicon in various countries. The materials used were selected from samples from Europe and America, the final choice depending on the geographical locality and the geological age of the silica used in the manufacture (Table II). A British sample was thought desirable, and the pegmatite mentioned below was used as a source of elementary silicon.

TABLE II.

Europe.

(a) 91·2% Ferrosilicon, smelted by the Gullspangs Elektrokemiska Aktiebolag, at Gullspang, Sweden, from quartzite obtained at Anenaset, W. of Lake Animmen, Sweden.

(b) 75% Ferrosilicon, smelted by Keller and Leleux, at Usine de Livet, Isère, from quartzite obtained at Bourg St. Maurice, Haute Savoie, France.

(c) Pegmatite from a vein 4·5 miles W. of Strontian, Scotland.

America.

(a) 50% Ferrosilicon, smelted by the Southern Ferro Alloys Company, Chattanooga, Tenn., from silica obtained from the sandstone cap of Lookout Mountain, Alabama, U.S.A.

(b) 90% Ferrosilicon, smelted by the Union Carbide and Carbon Products Company, Niagara Falls, from quartzite obtained at Killarney, Ontario, Canada.

The authors wish to record their grateful thanks to these and other firms and individuals in various parts of the world who have made this investigation possible by so courteously placing material and information at their disposal.

Preparation of Silicon Tetrachloride from Ferrosilicon.—Warren's method (*loc. cit.*) was subsequently elaborated by Martin (J., 1914, **105**, 2836), but preliminary experiments showed that these complications were largely unnecessary in the present case. Chlorination of the ferrosilicon was carried out in iron tubes 3 ft. by 1·5 in. which were dried by twice heating to redness in a combustion furnace and cooling with dry air passing through them. After a run they were thoroughly washed and redried, but the majority of the tubes were perforated after two, and none lasted beyond three, chlorinations. Ferrosilicon as a coarse powder retained on a 40-mesh sieve was found to be most suitable. This was obtained by crushing the material in a Weatherhead mill; it was then dried, at 110°, in charges of 200—300 g. immediately before being put into the tubes. The iron tube was heated by a silica-tube resistance furnace. Chlorine from a cylinder was led through two sulphuric acid wash-bottles, past a T-piece manometer dipping 8 inches into frequently renewed sulphuric acid, to the reaction tube. The products were led through an adapter into a clean dry receiving bottle, cooled in a freezing mixture and fitted with an exit tube leading to a ventilator shaft. A rapid stream of chlorine was passed through the heated tube, and after 25 minutes the production of silicon tetrachloride began, and when the rate of production diminished fresh ferrosilicon was exposed to the action of the gas by rotating the tubes slightly and tapping them. Occasional slight back-pressure, due to ferric chloride, was relieved in this way, but after 2·5—3·5 hours the tubes choked up completely and thus ended the run. About 700 c.c. of crude product were obtained from each source and

hermetically sealed by closing the bottle with a tied-in waxed cork.

Preparation of Silicon Tetrachloride from Pegmatite.—The pegmatite was rich enough in silicon to be treated as an impure specimen of the oxide, and was reduced with aluminium in the presence of sulphur (Holleman, *Proc. K. Akad. Wetensch. Amsterdam*, 1904, **1**, 189; Kuhne, D.R.-P. 147871). 200 G. of finely ground mineral were very thoroughly mixed with aluminium powder (200 g.) and flowers of sulphur (250 g.), charged into a No. 6 Battersea crucible, covered with a layer of sulphur, and fired by means of magnesium ribbon set in a primer of magnesium powder and barium peroxide. Immediately following the reaction, the hot crucible was plunged into water, the aluminium sulphide being thus decomposed, leaving nodules of crystalline silicon. These were washed, dried, crushed, and finely ground in a Weatherhead mill, and this powder was treated with concentrated hydrochloric acid, when there was a marked evolution of gas and a smell suggestive of a silicide. The wash-acid was heated to boiling, cooled, diluted with water and filtered through a Buchner funnel with the aid of a pump. The resulting moist mass was digested with 1 : 2 hydrochloric acid for some time, again filtered, well washed in the funnel, and dried at 110°. 300 G. of silicon as a fine, dark grey powder were obtained from nine reductions.

About 30 g. of this material were placed in a clean dry Jena glass tube of 0·75 in. bore and chlorinated as described for ferro-silicon. The silicon glowed during the chlorination and a small quantity of white residue remained. About 700 c.c. of product were obtained and bottled as before.

Rough Fractionation of Crude Silicon Tetrachloride.—This step was introduced to rid the crude product of most of its chlorine and all its solid impurities. The cork of the bottle containing the crude material was replaced by a waxed cork, provided with a short wide delivery tube, which was already connected by means of rubber to a specially constructed fractionating column, 2 ft. long, filled with glass beads. The bottle was carefully heated by a water-bath, and a small head fraction carrying most of the chlorine was allowed to go entirely to waste. A head fraction of about 70 c.c. was now collected in a small bottle cooled in a freezing mixture and, as the last third of this fraction ran colourless, it was concluded that the bulk of the chlorine had been removed. A main fraction of about 600 c.c. was then collected in a dry litre bottle, containing 40 c.c. of pure mercury : it was stoppered as previously described. A slight flouring of the mercury in the case of each main fraction indicated that a trace of chlorine was still

present.   The tail fractions subsequently yielded specimens of the hexachloride (b. p. 141·5°), and a fraction of higher boiling point that could not be driven up the column, which was, presumably, the octachloride.   The amounts of higher chlorides found were less than those obtained by Martin (*loc. cit.*) in his carefully regulated chlorinations.

Purification of Silicon Tetrachloride.

The importance of a rigorous purification need hardly be stressed. The crude material possibly contained :

Chlorine	b.p. −34°	Disilicon hexachloride	b.p. 145°
Hydrochloric acid	−83	Trisilicon octachloride	212
Phosphorus trichloride	76	Antimony trichloride	226
Arsenic trichloride	130		

Silicon dioxide and its hydrates are probably only very slightly volatile in the vapour of silicon tetrachloride.

Of these compounds, only phosphorus trichloride was likely to persist, but it has a boiling point 16·5° above that of silicon tetrachloride.   The methods available for purifying the liquid were fractional crystallisation and distillation, and contact with mercury and sodium.   Fractional crystallisation was originally part of the scheme, but, unfortunately, became impossible by reason of the increased difficulties experienced in obtaining supplies of liquid air. The means available were thus fractional distillation and prolonged contact with liquid sodium amalgam.   They were conducted in the following stages (see Fig. 1, where T, H, and M represent tail, head, and main fractions respectively) :

1. Rough fractionation through a single-column still.
2. Standing for 6 months over mercury, with frequent shakings.
3. Systematic fractional distillation in four stages, conducted in dry air at about atmospheric pressure in an all-glass four-column still.
4. Standing with frequent shakings for upwards of 2 months over sodium amalgam.
5. Fractional distillation into five fractions in a vacuum.
6. Fractional distillation into five fractions in a vacuum.

Main Fractionation of Silicon Tetrachloride at Atmospheric Pressure.—This was conducted in a 4-column still (Fig. 2) of Durosil glass similar in principle to that used in the purification of boron trichloride by Briscoe and Robinson (*loc. cit.*).   Each piece of the apparatus * was cleaned with chromic-nitric acid, washed with water, rinsed with pure alcohol, and allowed to drain.   The parts

* Our thanks are due to Mr. G. Ellison of this department for making the individual pieces of glass-ware used in this investigation.

were then assembled and dried by passing dry air in at M and out through T_1 for 3 days, the mercury in the valves sealing the apparatus from outside air. The capillary of the special joint was then sealed, and freshly-made sodium amalgam was filtered into M by means of a long-stemmed funnel. All exit tubes were bent to point downwards, so that any liquid condensing in the phosphorus pentoxide guard-tubes was unable to return to the apparatus.

About 600 c.c. of the roughly-fractionated crude product, after standing over mercury with repeated shaking for 5—6 months, were distilled into B_1, which was cooled in ice-cold water, leaving
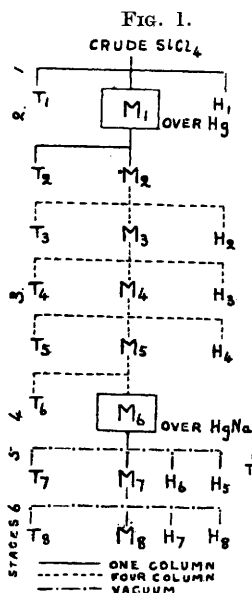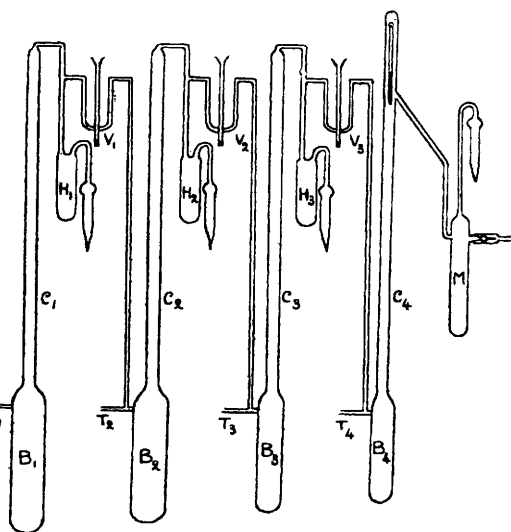
Fig. 1.

Fig. 2.

behind a tail fraction of 20 c.c. A paper jacket containing solid carbon dioxide kept the base of C_1 cool, while extra mercury which had been poured into V_1 cut off connexion between B_1 and B_2. T_1 was then sealed off. B_1 was gently warmed with a soft flame, as this method of heating gave steady boiling, and a head fraction of about 50 c.c. was distilled into H_1 which was cooled in solid carbon dioxide. This head fraction was sealed off, mercury was run from V_1 to establish connexion with B_2, and a main fraction of about 500 c.c. was distilled forward into B_2, which was cooled in iced water, the base of C_2 being jacketed with solid carbon dioxide. More mercury was poured into V_1 and the tip of T_1 was broken under rubber to connect with a phosphorus pentoxide tube, thus establishing equal pressures at both sides of the valve. A tail of

x x 2

about 50 c.c. remained in B_1.   Similar head and tail fractions
were rejected in distillations from B_2 and B_3, resulting in 300 c.c.
of material in B_4.   The liquid in B_4 was then distilled forward past
the thermometer into M (cooled in solid carbon dioxide) where it
was sealed up.   About 25 c.c. of liquid returned to B_4 on account
of column capacity.

To prepare the apparatus for the next distillation the tails and
drainings from the columns were distilled from the various boilers by
opening the side-tubes T_1, T_2, T_3, and T_4, after which these side-
tubes were sealed up and dry air was passed completely through
the apparatus for 3 or 4 days with occasional warmings, thus
removing the last traces of silicon tetrachloride : the new head-
bulbs were then fused on, and the apparatus carefully dried for
the next sample.

The Boiling Point of Silicon Tetrachloride.—This is a useful
criterion of purity, and it was measured with all the accuracy
possible under the conditions of the experiment.   The thermometer
used (range 10—60°) was subsequently compared with the N. P. L.
thermometer mentioned below, and was usually less than 0·02° in
error.   Temperatures, which remained fairly steady, were taken
at short intervals, any fluctuations being traceable to variations in
the rate of distillation which caused slight pressure changes in the
system.   There was absolutely no tendency towards a rise of
temperature during the last stages of each distillation.   Table III
gives the mean boiling point and atmospheric pressure for each
sample.

<div align="center">TABLE III.</div>

Sweden	57·10°	761·6 mm.	France......... 56·83°	753·9 mm.
Scotland	56·95	758·0 mm.	Canada ...... 56·91	756·0 mm.
U.S.A.	57·12	763·3 mm.		

This indicates a boiling point between 57·02° and 57·05° at 760 mm.,
a figure in fair agreement with the 56·9° of Becker and Meyer (*loc.
cit.*) and the 56·8° of Stock, Somieski, and Wintgen (*Ber.*, 1917,
50, 1754).

[*Special Note on the French Fraction.*—A few days after distillation
the vessel containing the main fraction of the French material
from the 4-column still developed an extensive series of cracks
round the upper portion near the special joint.   Since there was
no apparent entry of air into the container, it was painted over
with thick collodion varnish, bound with pure rubber tape and
finally painted with a viscous solution of pure rubber.   After
standing for some days, it was joined to a new, clean, dry special-
joint container provided with fresh sodium amalgam, the strains
between the two vessels being relieved by a number of right-angle

ends in the thin-walled connecting tube. The special joint was
hen broken, and, with the exception of about 10 c.c., the liquid
vas poured into the new vessel, the exit tube of which carried a
)hosphorus pentoxide guard-tube.]

First Vacuum Distillation of Main Fractions.—The containers,
1olding the five main fractions from the 4-column still, were severally
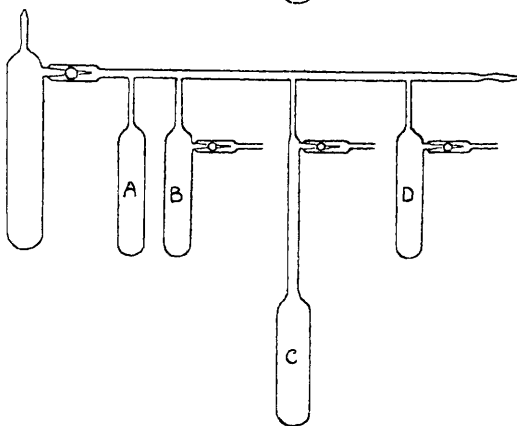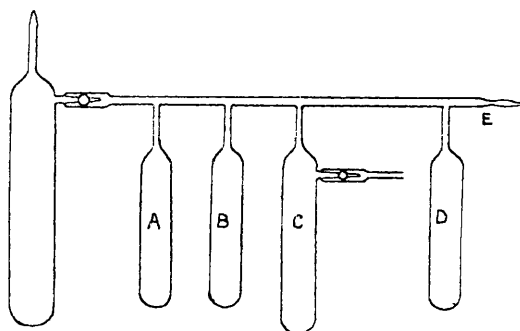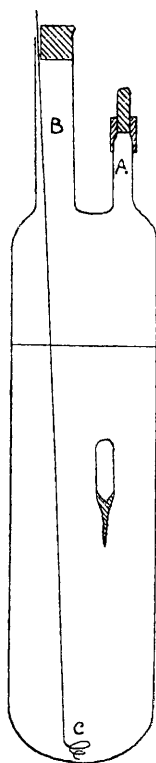sealed to trains (Fig. 3) consisting of a small head-bulb A and

FIG. 3.   FIG. 5.

FIG. 4.

containers, B for the head fraction proper, C provided with a
special joint for the main fraction, and D for the tail fraction. The
train was evacuated five times while at about 120°, being each time
slowly filled with dry air, and finally allowed to cool under atmo-
spheric pressure. The silicon tetrachloride was cooled with liquid
air to near its freezing point, and the capillary of the special joint
was broken with the train at atmospheric pressure though still
protected from moisture by the drying train. It was evacuated

and sealed off at E when the manometer registered less than 2 mm. pressure. (In the course of these distillations it was observed that solid silicon tetrachloride at very low pressures retained permanent gas which was disengaged when the solid melted.) A small head fraction of about 10 c.c. was collected in A which was sealed off, and a head fraction of 50 c.c. was distilled into B. A main fraction of about 150 c.c. was collected in C and a tail of about 50 c.c. in D, the amalgam in the original container being left quite dry.

The " hammer " of silicon tetrachloride in a vacuum at temperatures near its freezing point was considerable enough to render cautious handling absolutely necessary.

Second Vacuum Distillation of Main Fractions.—This was carried out after fusing to the train the main fraction containers obtained above (Fig. 4). The material was now so pure that head and tail fractions were worth preserving, and thus B and D, in addition to C, had special joints. C was specially constructed with a long neck so that it could be introduced into a water-bath, and before fusing on, into it were placed the two floats to be used subsequently in determining the density of the liquid. Very special precautions were taken in the washing and drying of the whole apparatus before the final evacuation : before the various parts were actually fitted together, each piece was treated with chromic–nitric acid for about 12 hours, well washed with tap water, then with ordinary distilled water, and finally with pure alcohol and ether and left to dry. On the day before assembling, each piece was treated with four large washings of special distilled water, followed by two with pure dry alcohol and two with pure ether. In assembling, the vessels which had to be sealed off during the course of the fractionation were held by clamps lined with asbestos paper—a provision which entirely prevented the sticking of cork and glass by repeated heating.

Each complete train was tested on the pump, and any minute leaks, which occasionally occur in such a high-melting glass as Durosil, were fused up. When finished, the apparatus was heated to about 120°, twice evacuated and slowly filled with dry air, and allowed to stand overnight protected by a new phosphorus pentoxide guard-tube. It was then evacuated six times with heating and slow refilling with dry air, the final evacuation, lasting 30 minutes, being made with the whole of the glass as near 200° as possible, and the manometer recording zero pressure when the apparatus was sealed off from the pump.

In distilling, the procedure was first to cool the whole of A with liquid air, at the same time heating C to 120°, and thus to remove any moisture from the surface of C and deposit it in A. With

these conditions still obtaining, the special joint was broken, and *instantly* a snow of solid silicon tetrachloride covered the surface of A, thus fixing any moisture and retaining it in that part of the apparatus. Further cooling was at once applied, and in about 5 minutes a small head fraction (6—9 c.c.), most of the residual air, and probably all the products of hydrolysis, if any, were removed from the system by sealing off A. This was followed by a head of about 30 c.c. in B, a main of about 60 c.c. in C, and a tail fraction of about 30 c.c. in D, leaving the original vessel dry and with the merest trace of white residue, which was greatest in the French and least in the Scottish sample. During the distillations into A and B the container C was kept warm, and the greater part of most of the distillations took place at below 0° as shown by a coating of ice on the outside of the vessels.

Before introducing them into C, the floats were gently polished with clean, well-washed linen, and a careful record was made of the destination of each float.

The Preparation and Standardisation of the Floats.

Since no method of density determination which involved exposure to air could be used with silicon tetrachloride, recourse was had to the use of glass floats. This method appeared likely to give results of much greater comparative accuracy than the older means, and actually proved to do so. It involved the preparation of two sets of floats with densities slightly above and slightly below the density of the liquid at the proposed temperature of the measurement; the determination of the relative density of these to the highest degree of accuracy attainable; and finally the observation of the flotation-temperature of pairs of these floats in the various specimens of liquid under examination. Thus, at these two temperatures the density of the liquid was known, and could be calculated very accurately at an intermediate temperature provided the interval was small. The use of two floats gave the necessary information as to the coefficient of thermal expansion of the liquid.

Construction of Floats.—Floats were made from thin-walled Durosil glass tubing of about 3 mm. external diameter and were of the form shown in Fig. 5. The barrel was about 12—15 mm. long, and the solid tail, which was about the same length, was in the form of a long taper. The finished floats had a smooth surface without any indentations which might serve as a place of lodgment for small bubbles. Large numbers were made and those for final adjustment were chosen by elimination. The final adjustment of the two sets was made using bromobenzene at constant temperatures

of 22·5° and 29·5°, respectively, and small amounts of glass were added to, or removed from the tails of the floats until their densities very closely approximated to that of the liquid at one of these temperatures. The magnitude of this apparently simple task will be recognised when it is remembered that 1·0° difference in flotation temperature is equivalent to about 0·001 density unit.

These bromobenzene temperatures had been chosen after comparing the flotation-temperatures of three floats in fairly pure silicon tetrachloride and then in the bromobenzene.

Determination of the Density of the Floats.—The density of the floats was determined by ascertaining very precisely the flotation-temperature of each float in a liquid, the density of which was afterwards determined at that particular temperature. It was realised that for the present purpose high accuracy in relative density was more important than the absolute value.

The ideal flotation-liquid would be a pure substance stable in air, non-hygroscopic, of comparatively high boiling point and having a density and a coefficient of thermal expansion about those of silicon tetrachloride. Bromobenzene approaches this ideal very closely; its density is 1·494 at 20° (Young, *Journ. de Phys.*, 1909; Perkin, J., 1896, **69**, 1202); its coefficient of expansion is very near that of silicon tetrachloride, 1° change in temperature altering the densities to the extent of 0·0010 and 0·0011 unit, respectively, and its boiling point is 156° (Young, *loc. cit.*). The material first used was as supplied by The British Drug Houses, Ltd., since absolute purity seemed to be immaterial, but after it had been in use for some days a redetermination of the flotation-temperatures of three floats indicated that the liquid was changing in density (see Table IV). The liquid was therefore redistilled with the

TABLE IV.

Float.	1st Flotation-temp.*	2nd Flotation·temp.*	Difference.
C	20·735° (Oct. 30th)	20·765° (Nov. 4th)	0·030°
D	20·635 ,,	20·650 ,,	0·015
H	20·730 (Nov. 2nd)	20·758 ,,	0·028

* Not corrected for exposed stem.

rejection of considerable head and tail fractions. The main fraction gave a very constant boiling point (155·4°/754·1 mm.), and if the distillate was not now chemically pure, it was at least composed of substances not readily separated by the conditions obtaining during the flotation tests. The distilled liquid was exposed to the atmosphere for 7 days, being adequately protected from dust, in order to acquire a normal moisture content. A redetermination

of the flotation-temperatures of Floats C, D, and H indicated that the density of the liquid had changed considerably (Table V).

TABLE V.

Float.	2nd Flotation-temp.*	3rd Flotation-temp.*	Difference.
C	20·765°	25·856°	5·091°
D	20·650	25·736	5·086
H	20·758	25·838	5·080

* Not corrected for exposed stem.

On November 12th and 13th a complete set of flotation-temperatures was obtained, this being followed by the determination of the density of the liquid, and between November 17th and 20th another complete set was added. The second set showed a fall, varying between 0·007° and 0·020°, increasing with the passage of time throughout the 3 days, indicating a fall in density of the liquid which was attributed to the further absorption of moisture from the atmosphere.

The flotation-vessel was of Durosil glass in the form shown in Fig. 5, the body being about 3·5 cm. by 16 cm., and was about three-quarters filled with liquid. A was a narrow tube normally closed by a rubber cap, while B was a wider opening through which the floats were introduced and removed, and which was closed by a small cork with a groove for the passage of the float-lifter, C. This was made of No. 19 S.W.G. nichrome wire carefully cleaned and polished, and appeared to suffer no attack by the liquid. The spiral at the end served to hold the floats in a vertical position during their passage through B. The floats were handled carefully by means of nickel-plated forceps and were polished by clean, well-washed linen on entering and leaving the liquid. The wire was not lifted farther out of the liquid than was absolutely necessary and was allowed to fall back into its place after use; and, except when changing floats, B was corked and protected from dust by an inverted test-tube D. Thus every endeavour was made to ensure the permanence of the liquid during the period of the flotation-tests.

The temperature of the flotation-liquid was regulated by submerging the vessel in a tank of square cross-section holding about 27 litres of water and having large plate-glass windows at the front and back. The bath was provided with a large, mechanically-driven, propeller-shaped stirrer, an electric heater consisting of a nichrome element inside a vitreosil tube, and a cooling coil consisting of several turns of $\frac{3}{8}$-inch "compo" gas-piping connected to the ordinary water supply which, at the particular season of the year in question, was cold enough.

X X*

The thermometers used were : (a) Thermometer 1—a special open-scale thermometer reading from $+ 9.5°$ to $+ 25°$, graduated in $0.02°$ and easily read to $0.005°$; (b) Beckmann I; (c) Beckmann II. In use, the bulb of each thermometer was about 8 inches below the surface of the water and the portion remaining was surrounded by a jacket containing water in which was a second ordinary thermometer giving the stem temperature. The observed temperature was corrected by means of the usual formula $s = an(T — t)$ with $a = 0.000143$ (Thorpe, J., 1880, **37**, 160). Thermometers (a) and (b) were set in definite relationship, the permanence of the setting being tested from time to time, and, finally, each of the three thermometers was carefully compared with a $0°$—$50°$ open-scale thermometer, graduated in $0.02°$, and recently calibrated at the National Physical Laboratory to $0.01°$ at each degree. All temperatures were thus accurately converted from the various arbitrary scales into degrees Centigrade.

Two methods suggested themselves for the purpose of obtaining flotation-temperatures : (a) by maintaining such a temperature that the float remained balanced in the liquid for a considerable period, say 20—30 minutes; (b) by making such slight variations in temperature as would cause the floats to rise or fall, and to take the mean of the last closely-agreeing pair of readings as the flotation-temperature. As some of the temperatures were $15°$ above that of the air in the room, the static method presented considerable difficulties in maintaining a constant temperature and, furthermore, failed to disclose any lag between flotation-liquid· and bath temperatures. The second method was, therefore, adopted and was later modified by taking the mean of a number of *rise* and *fall* temperatures, and, by a series of time–temperature readings, ascertaining the rate at which the temperature of the bath varied. No useful purpose would be served in giving in detail all the readings from which the flotation-temperatures were ultimately derived, but a general idea of the accuracy may be obtained from the fact that out of 40 flotation-temperatures, 6 were derived from values $0.005°$ apart, 24 from values $0.010°$ apart, and 9 from values $0.015°$ apart.

The density of the flotation-liquid (bromobenzene) was determined at $25.655°$, $25.666°$, $33.213°$, and $33.210°$, the same pyknometers and method of filling being used as already described in a recent publication (Briscoe, Robinson, and Stephenson, *loc. cit.*), and only the special precautions taken to secure accuracy need be mentioned here. The pyknometer was weighed against a tare with calibrated weights on a No. 7 S.W. Oertling balance with a sensitivity of 21 divisions per mg. The vacuum weight of the

pyknometer was calculated from three separate weighings before, during, and at the conclusion of the determination, and its absolute volume was obtained by duplicate water-fillings at the two temperatures and the use of the value for the specific volume of water (Kaye and Laby, " Physical and Chemical Constants," 1911, p. 22). The liquids were delivered into the pyknometer at as near the correct temperature as possible; then the vessel was held in the bath at about 0·10° below the required temperature for upwards of 30 minutes, after which heat was gently applied and the temperature maintained for about 5 minutes at 0·01° below and then finally raised to the required temperature. In order to eliminate both speculation and observational error the temperature at the latest stage was taken at half-minute intervals and when it had remained fixed for about 4 minutes the setting was made. These temperatures were probably less than $\pm$ 0·001° in error and their accuracy was far beyond that justified by the precision of the pyknometer setting. The densities (g. per c.c.) of the flotation liquid are in Table VI, where some corresponding values by Perkin (J., 1896, **69**, 1202) are given for comparison.

TABLE VI.

t.	d.	d (Perkin).	
25·665°	1·48766	25°/25°	1·4886
33·210	1·47741	30 /30	1·4841
		35 /35	1·4798

The flotation-temperatures (corrected for exposed stem) determined before and after the density work are in columns 2 and 3 respectively of Table VII, while in column 4 are the absolute flotation-temperatures derived from column 2 by the application of the calibration correction. The densities of the floats (in g. per c.c.) calculated by assuming a straight-line relationship between density and temperature over the 7·6° range are in column 5.

TABLE VII.

Float.	2nd Flotation-temp.	3rd Flotation-temp.	Absolute Flotation-temp.	d.
D	25·751°	25·736°	25·746°	1·487550
A	25·855	25·848	25·850	1·487407
E	25·849	25·841	25·844	1·487416
H	25·851	25·838	25·846	1·487413
C	25·866	25·858	25·861	1·487393
Q	32·933	32·915	32·950	1·477734
M	32·943	32·933	32·960	1·477721
L	33·013	33·003	33·028	1·477628
K	33·063	33·043	33·082	1·477554
I	33·073	33·048	33·092	1·477541

x x* 2

The Density of the Five Samples of Pure Silicon Tetrachloride at 20°.

The flotation-temperatures of the two floats in the various samples gave data for the calculation of the densities of the liquids at 20·000° and their coefficients of expansion over the range 17·1° to 21·7°. In this case again a straight-line relationship was assumed over the 4·6° range.

The peculiar behaviour of the floats in silicon tetrachloride calls for comment, if for no other reason, because of the trouble it gave. The main fractions were removed from the fractionating train almost entirely in the solid condition; on the solid melting, the released floats came to the surface, and when the liquid attained room temperature (18—20°) one in each case went slowly to the bottom : in brief, the floats moved quite normally in the liquid, but with a greater velocity than in the bromobenzene for an equal temperature change on account of difference in viscosity. It was found, however, that movement of the liquid in the vessel, by shaking or even by the tremor set up by a small motor running on the same bench, caused each float to assume a positive electrical charge. These charges have not yet been completely investigated, but they were sufficient at the time to cause the floats to stick so firmly to the side of the vessel that only the most violent shaking could dislodge them, and then only for the moment, for, once released, they immediately stuck fast elsewhere. The charges gradually decreased in magnitude with the passage of time, but they were easily acquired again and evidence up to the present appears to indicate that they are not lost completely after a period of several weeks, though they may be so small as not to affect the movement of the floats.

The Flotation-Temperatures in Silicon Tetrachloride.—To avoid any tremor in the liquid the water·bath was fitted up in a room reserved for the purpose : the permanent, wall-side bench carried the bath, with stirrer, etc., while in front of this bench, but not touching it, was a small, absolutely steady, heavy table on which was the retort-stand carrying the container, the body of which was submerged 1·5 to 2 inches below the surface of the water. It was found that when the floats had very little charge they left the side or bottom with extreme readiness when the density was reached, and that once in the centre they could be made to go up and down several times without touching the side, surface, or bottom. When the charge was slightly greater, the floats could be dislodged by giving the retort-stand a smart tap, and when once moving even these floats could be made to go up and down several times before attaching themselves to the sides again. When the behaviour of the floats was worse than this, the container was

removed from the bath and allowed to stand for several days without disturbance. In all, 105 rising and falling temperatures were taken on the ten floats, and concordant repetitions had to be obtained before the values were accepted, but this checking, whilst it ensured absolute satisfaction, was in reality hardly necessary, for, invariably, once a float was moving freely it gave concordant results, whereas the presence of a charge too great to allow of proper freedom was immediately evident. It is probable that these flotation-temperatures in spite of the above difficulty were, by reason of increased experience and the reduced viscosity of the liquid, more accurate than the earlier ones taken in bromobenzene. Table VIII gives these flotation-temperatures in respect of each float, the corresponding density of the liquid at that temperature, and the calculated density at 20·000°.

<div align="center">TABLE VIII.</div>

Source.	Float.	Flotation-temp.	d at flotation-temp.	d at 20°.
Canada	$\begin{cases} E \\ K \end{cases}$	17·044° 21·757	$\left.\begin{array}{c} 1·487416 \\ 1·477554 \end{array}\right\}$	1·481231
U.S.A.	$\begin{cases} D \\ M \end{cases}$	16·969 21·683	$\left.\begin{array}{c} 1·487550 \\ 1·477721 \end{array}\right\}$	1·481230
Sweden	$\begin{cases} C \\ I \end{cases}$	17·046 21·763	$\left.\begin{array}{c} 1·487393 \\ 1·477541 \end{array}\right\}$	1·481223
Scotland	$\begin{cases} H \\ L \end{cases}$	17·046 21·748	$\left.\begin{array}{c} 1·487413 \\ 1·477628 \end{array}\right\}$	1·481266
France	$\begin{cases} A \\ Q \end{cases}$	17·062 21·695	$\left.\begin{array}{c} 1·487407 \\ 1·477734 \end{array}\right\}$	1·481273

<div align="center">*Discussion of Results.*</div>

The Densities.—The densities of silicon tetrachloride above have an extreme variation of 0·000050, and have a mean value of 1·481245. A careful review of the method leads to the belief that these densities have a relative accuracy greater than $\pm 0·000005$, but their absolute value is more difficult to assess because it is based on the densities of bromobenzene, and these may possibly deviate as much as $\pm 0·0002$ from the truth but probably not more than this. Unless the errors in the densities of bromobenzene at the upper and lower temperatures respectively are both in the same direction, their effect will be reduced in the process of computation and the absolute density of the floats is likely to be less than $\pm 0·0002$ in error, whilst in the same way the calculation used to arrive at the density of the silicon tetrachloride probably further diminishes the error here. Thus the density of silicon tetrachloride under the pressure of its own vapour (*i.e.*, 21 mm., Becker and Meyer, *loc. cit.*; Regnault, *Mem. Acad.*, 1826, **26**, 476) at 20·000° $\pm$ 0·0005° is 1·481245 $\pm$ 0·00005. This figure bears little

relationship to the previous results given below, and the reasonable presumption is that the material used by these workers was of doubtful purity.

Koster, *Jahresber.*, 1826, **6**, 120 .... 1·54
Pierre, *Ann. Chim. Phys.*, 1847, **20**, 27 .... 1·52371 at 0°
Mendeléeff, *Compt. rend.*, 1860, **51**, 96 .... 1·4928 at 15°
Friedel and Crafts, *Ann. Chim. Phys.*, 1866, **9**, 5 .... 1·522
Haagen, *Pogg. Ann.*, 1867, **131**, 122 .... 1·4878 at 20°
Thorpe, *Ber.*, 1876, **9**, 509 .... 1·52408 at 4°
Abati, *Gazzetta*, 1897, **27**, 437 .... 1·47556 at 22°
Stiefelhagen, *Dispersion Flüssiger Trichloride und Tetrachloride*
    für ultraviolette Strahlen, Berlin, 1905 .... 1·524 at 16°
Ruff and Albert, *Ber.*, 1905, **38**, 53, 2222 .... 1·4933 at 15°

The Coefficients of Thermal Expansion.—The figures given in Table VIII may obviously be used to calculate the coefficient of thermal expansion of the liquid. There seems to be no *a priori* reason for supposing that a slight difference in the isotope ratio should have any effect on this physical constant; furthermore, this constant is in a measure independent of the density determination, depending as it does upon the temperature interval only and not upon the actual readings giving the interval, and it should therefore afford an excellent check upon the soundness of the method. These coefficients of thermal expansion are given in Table IX, in which, for ease of comparison, the densities also are recorded. The former have an extreme variation of 0·0000080, and a mean value of

TABLE IX.

Source.	Density.	Diff. from mean.	Coeff. of expansion.	Diff. from mean.
Canada	1·481231	− 0·000014	0·0014163	+ 0·0000039
U.S.A.	1·481230	− 0·000015	0·0014109	− 0·0000015
Sweden	1·481223	− 0·000022	0·0014136	+ 0·0000012
Scotland	1·481266	+ 0·000021	0·0014083	− 0·0000041
France................	1·481273	+ 0·000028	0·0014129	+ 0·0000005
Mean	1·481245	± 0·000020	0·0014124	± 0·0000022

0·0014124, which has an error probably less than ± 0·0000022. This figure is decidedly lower than the previous determinations, 0·001430, due to Pierre (*Ann. Chim. Phys.*, 1851, **33**, 241), and 0·001446, due to Thorpe (*Proc. Roy. Soc.*, 1876, **24**, 283). Without criticising the methods of the earlier workers, it will suffice to examine briefly the basis of the present determinations, *viz.*, the density and temperature intervals. The density interval depends on the densities of bromobenzene at the two temperatures : the greater the density difference the greater the coefficient of expansion indicated. Reference to p. 1277 will show that the difference in density for the given interval of temperature, 7·545°, is 0·01025 unit, whilst Perkin (*loc. cit.*) found for 10° a difference of only

0·0088 unit. Thus if Perkin's densities had been used the resulting coefficients would have been still lower. Enough has been said about flotation-temperatures to make it clear that considerable confidence may be placed in results based on them. The concordance shown by the results lends additional weight to the suggestion that they should be accepted with complete rejection of the previous data.

As criteria of the accuracy of the densities it is important to note that considerable departure from the mean seems to alternate between density and expansion in each case except in the sample from Scotland. The sample from Sweden shows the best figures. The table indicates that the causes producing the deviations are acting fortuitously, and that the errors are evenly and accidentally distributed. Thus a consideration of either column increases confidence in the other.

The Relative Atomic Weights.—Taking 1·481245, the mean density of the various samples, as equivalent to Si = 28·060, the atomic weights corresponding to the various densities found are set out in Table X.

<div align="center">TABLE X.</div>

Origin.	Density.	At. wt.	Origin.	Density.	At. wt.
Canada	1·481231	28·059	Scotland	1·481266	28·062
U.S.A.	1·481230	28·059	France	1·481273	28·063
Sweden	1·481223	28·058	*Mean*	1·481245	28·060

Assuming the relative accuracy of the densities given above, these are capable of indicating changes in the atomic weight of the order of 0·001 unit, and it may reasonably be asked whether they are actually doing so here. The high value found for the French sample may perhaps be explained by the cracking of the container (see p. 1270)—a view which gains support from the observation subsequently made (see p. 1273) that this sample yielded the greatest trace of residue in the second vacuum distillation. Nothing is known against the sample from Scotland, but the considerable deviation of the coefficient of thermal expansion from the mean is probably not without significance. The evidence indicates that no greater variation than 0·005 unit in the atomic weight is to be expected in the samples of silicon under consideration.

The Use of Floats Generally.—It has been shown that carefully calibrated floats are capable of giving densities of liquids to a very high degree of accuracy, but it is also clear that the method could be greatly refined now that a knowledge of the technique has been obtained. To just what limit the method could be extended is not yet known. It has the advantage, however, of being applicable to any liquid which does not attack glass or silica, and may

be used to determine the coefficients of expansion and compressibility, and to follow the changes in liquids undergoing treatment in closed vessels.