CXXII.—The Atomic Weight of Vanadium.

By HENRY VINCENT AIRD BRISCOE and HARRY FRANK VICTOR LITTLE.

FEW determinations of the atomic weight of vanadium have been made, and the results are by no means concordant. The early experiments of Berzelius (Pogg. Ann., 1831, 22, 14) and Czudnowicz (ibid., 1863, 120, 17) may now be disregarded, as they are only of historical interest. The first determinations of any scientific value were those carried out by Roscoe in the course of his classic researches on vanadium (Phil. Trans., 1868, 158, 1; this Journ., 1868, 21, 322). Three ratios were measured, namely, $V_2O_5 : V_2O_3$, $VOCl_3 : 3Ag$, and $VOCl_3 : 3AgCl$. The measurement of the first was effected by reducing a weighed quantity of vanadium pentoxide to vanadium sesquioxide at a red heat in a stream of pure dry hydrogen and determining the diminution in weight. The second ratio was determined by breaking a sealed glass bulb containing a known weight of vanadyl trichloride in a stoppered bottle containing a solution of silver nitrate. The latter had been prepared by dissolving almost the necessary amount of silver in nitric acid and diluting with water. The additional silver required to complete the titration was then added in small quantities at a time according to the method of Stas. The third ratio was measured in a similar manner to the second, but the silver chloride produced was collected, dried, and weighed.

Roscoe's results may be stated as follows *:

 $V_2O_3 : V_2O_5 : : 1 : x.$

5	Experiments-	
	x = 1.21261 (highest) x = 1.21196 (lowest) x = 1.21225 (mean)	$V = 51 \cdot 256$ $V = 51 \cdot 486$ $V = 51 \cdot 382$

^{*} The antecedent data used throughout this paper are as follows :

O=16, Ag=107.880, Na=23.000, Cl=35.460 and 35.457, results corresponding with each of these two last values being given.

 $VOCl_3 : 3Ag : : x : 1.$

9	Experiments-		Cl = 35.460.	(2l = 35.457
	x = 0.53980 (highest)	•••••	$V = 52 \cdot 321$	\mathbf{or}	$52 \cdot 330$
	x = 0.53425 (lowest)		V = 50.525	or	50.534
	$x = 0.53586 \text{ (mean)} \dots$	••••••	V = 51.046	or	51·055
	V	OCl ₃ : 3AgCl : :	x=1.		
8	Experiments—		Cl=35.460.	C	$1 = 35 \cdot 457.$
	x = 0.40537 (highest)	•••••	V = 51.937	or	51.943
	x = 0.40174 (lowest)		V = 50.376	or	50.382
	x = 0.40378 (mean)	••••••	V=51°253	\mathbf{or}	51 [.] 259

More than forty years after the completion of Roscoe's work, Prandtl and Bleyer (Zeitsch. anorg. Chem., 1909, **65**, 152; 1910, **67**, 257) published a re-determination of the atomic weight of vanadium. Their first experiments consisted in the measurement of the ratio $VOCl_3 : 3AgCl$, and were given in two series, referring presumably to two different samples of vanadyl trichloride. The results are summarised below:

 VOCl_3 : 3AgCl: : x : 1.

Series 1. 4 Experiments—	$Cl = 35 \cdot 460.$	C	$ \begin{array}{r} l = 35 \cdot 457. \\ 51 \cdot 212 \\ 51 \cdot 019 \\ 51 \cdot 139 \end{array} $
x=0.40367 (highest)	V = 51 \cdot 206	or	
x=0.40322 (lowest)	V = 51 \cdot 013	or	
x=0.40350 (mean)	V = 51 \cdot 133	or	
Series 2. 5 Experiments— x=0.40325 (highest) x=0.40287 (lowest) x=0.40311 (mean)	$V = 51.026 \\ V = 50.862 \\ V = 50.965$	or or or	51.032 50.868 50.971

With these results Prandtl and Bleyer appear to have been dissatisfied. Accordingly, eight new determinations were made, but four of the results were rejected as being defective. The others may be summarised as follows:

Series 3. 4 Experiments—	Cl = 35.460.	0	$21 = 35 \cdot 457.$
x = 0.40356 (highest)	$V = 51 \cdot 159$	or	$51 \cdot 165$
x = 0.40335 (lowest)	V = 51.069	or	5 1·07 5
x = 0.40346 (mean)	V = 51.116	\mathbf{or}	51 122

Thus Series 3 confirmed the results obtained in Series 1. Regarded as a single series of thirteen experiments, Prandtl and Bleyer's determinations give the following mean result:

 $\begin{array}{c} VOCl_{s}: 3AgCl:: 0.40335: 1\\ \therefore V=51.069 \quad (Cl=35.460),\\ v=51.074 \quad (Cl=35.457). \end{array}$

In addition to the preceding experiments, Prandtl and Bleyer carried out four determinations of the ratio $V_2O_3 : V_2O_5$, with the following results:

$\mathbf{v}_2\mathbf{v}_3$. $\mathbf{v}_2\mathbf{v}_5$	
x = 1.21259 (highest)	$V = 51 \cdot 261$
x = 1.21222 (lowest)	V = 51.395
x = 1.21233 (mean)	V=51 [.] 356

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These results agree well with those of Roscoe.

In a determination of the atomic weight of vanadium, published in 1910, McAdam (J. Amer. Chem. Soc., 1910, **32**, 1603) used a method totally different from any of those hitherto mentioned. A known weight of anhydrous sodium metavanadate, contained in a quartz flask, was heated in a stream of hydrogen chloride and chlorine, and the residual sodium chloride fused and weighed. The results were as follows:

 $NaVO_3: VaCl:: 1: x.$

5 Experiments-	Cl = 35 460.	C	$l = 35 \cdot 457.$
x = 0.47941 (highest)	$V = 50 \cdot 42$	or	50.936
x = 0.47921 (lowest)	V = 50992	or	50 ·986 (
x = 0.47932 (mean)	V = 50.966	or	50.960

It will be clear from the preceding résumé that there is room for considerably more work upon the atomic weight of vanadium. Simple though the oxide method may appear to be, the results it has afforded up to the present time must be regarded with considerable suspicion. The atomic weight derived from it is undoubtedly too high, and, according to Prandtl and Bleyer, is of little or no significance, since vanadium sesquioxide so readily absorbs oxygen, even at the ordinary temperature, that the determination of its weight is a matter of great difficulty. All the more obvious sources of error attaching to the method, namely, presence of non-volatile impurity, incomplete reduction of the vanadium pentoxide, and absorption of oxygen by the sesquioxide prior to the determination of its weight, cause the atomic weight deduced to be in excess of the true value. It may be mentioned as a curious and suggestive fact that many atomic-weight determinations carried out by effecting the analyses or syntheses of oxides are only of moderate value.

The vanadyl trichloride ratios of Roscoe and of Prandtl and Bleyer are evidently only approximations to the true values. Although the experiments of Prandtl and Bleyer are more concordant than the early experiments of Roscoe, yet their thirteen values for the ratio $\text{VOCl}_3: 3\text{AgCl}$ range from 0.40367 to 0.40287, numbers which differ by 1 part in 500, and the corresponding values for the atomic weight of vanadium vary from 51.21 to 50.87, a difference of more than three-tenths of a unit.

The disagreement between series 2 of their experiments and series 1 and 3 indicates that in some part of the work the vanadyl chloride analysed must have been impure, whilst the moderate agreement of the individual results indicates appreciable error, either in the method of analysis adopted or in the execution of the analyses.

The vanadate-chloride ratio determined by McAdam, however,

would appear to be of considerable value. The experiments were carried out with four different preparations of sodium metavanadate, and the fairly close agreement of the results leaves little room for doubt that this salt is so well defined as to be completely suitable for use in atomic weight work. Further, McAdam's method has the great advantage over the oxide method that the final substance weighed (sodium chloride) is, like the initial substance, a well-defined compound which can be fused without decomposition and readily examined for possible impurities. The experimental method is simple, and avoids transference of material. Hence, although McAdam regards his experiments as preliminary to a more detailed investigation, as yet unpublished, the atomic weight deduced from them should presumably be a fairly close approximation to the true value. It is accordingly noteworthy that all McAdam's values lie below 51.

Outline of the Present Investigation.

Although vanadium forms many compounds, few of them appear to be suited for use in the determination of its atomic weight; thus, McAdam states that the only vanadate of sodium that can be prepared of sufficiently definite composition is the metavanadate. Of the silver salts only the pyrovanadate appears to offer any promise, and when it is recalled that even such a salt as silver orthoarsenate is by no means easy to prepare in a state of purity (Baxter and Coffin, J. Amer. Chem. Soc., 1909, **31**, 297) it is at least doubtful whether an investigation of the composition of silver pyrovanadate would yield results of sufficient definiteness to compensate for the necessary expenditure of time and labour.

In the present investigation, therefore, the composition of vanadyl trichloride has been re-determined. The experimental difficulties arise from the nature of this substance, which is a liquid boiling at 127°, instantly decomposed by water into vanadic and hydrochloric acids, and must, therefore, be weighed in sealed glass bulbs. It was in devising a method by which the vanadyl trichloride could be fractionally distilled and collected in bulbs that the greatest difficulty was encountered.

Roscoe's method of effecting the analysis, already outlined (p. 1310) is inadvisable, since occlusion of soluble salt by the precipitated silver chloride undoubtedly occurs; the decomposition of the vanadyl trichloride and precipitation of the silver chloride must accordingly be effected in two successive stages.

Another possible source of error in Roscoe's method was pointed out by Prandtl and Bleyer. Vanadic acid is reduced by concentrated hydrochloric acid to vanadyl dichloride, chlorine being evolved, and the possibility of the liberation of a little free chlorine when vanadyl trichloride reacts with water must accordingly be recognised. To ensure the conversion of any free chlorine thus liberated into soluble chloride, Prandtl and Bleyer broke the bulb of vanadyl trichloride in a stoppered bottle containing water and a slight excess of zinc. The latter reacted with the hydrochloric acid and with any free chlorine which might have been produced, and reduced the vanadic acid to vanadyl dichloride.

It appeared probable to the authors that in cold dilute aqueous solution hydrochloric acid would be without action on vanadic acid, and a test experiment proved that such was indeed the case. Carbon dioxide was slowly bubbled for twenty-four hours through a dilute solution containing vanadic, hydrochloric, and nitric acids, and the issuing gas was passed through a solution of potassium iodide, the apparatus being constructed entirely of glass. No iodine was liberated.* Accordingly Prandtl and Bleyer's method of decomposing the vanadyl trichloride was rejected, and instead, the bulb containing the liquid was broken in a stoppered bottle containing a slight excess of an aqueous solution of ammonia. All the chloride was thus converted into ammonium chloride. The solution was diluted, cooled to 0°, acidified with nitric acid, and the chloride straightway precipitated by the addition of silver nitrate. The entire process thus resembled that adopted by Baxter and his collaborators in their analyses of phosphorus tribromide and phosphorus trichloride (J. Amer. Chem. Soc., 1912, 34, 259, 1644).

Of the two ratios that may be measured, namely, $VOCl_3 : 3Ag$ and $VOCl_3 : 3AgCl$, only the first was studied in detail. Two measurements of the second ratio were, however, also effected. The determination of the first of these ratios is considerably simpler than that of the second, and so affords less opportunity for the introduction of experimental errors; the results obtained by the two methods are, nevertheless, in excellent agreement.

The Preparation and Purification of Reagents.

Water.—The distilled water of the laboratory was of a high degree of general purity. In particular, repeated nephelometric tests made at frequent intervals throughout the whole course of the work showed it to contain an amount of chlorine never exceeding the equivalent of 0.03 mgm. of silver per litre of water. This water was used in the preparation of sample 1 of silver.

^{*} In this experiment the concentrations of vanadic, hydrochloric and nitric acids were chosen to correspond with those in the solutions obtained in the course of the analyses described later (p. 1327).

The water employed in the remainder of the work was prepared from the laboratory distilled water by distillation from a copper boiler of 25 litres capacity, after addition of a small amount of pure sodium carbonate. The steam was taken sideways from a done at the top of the boiler and passed through 60 cm. of 5 cm. copper pipe before entering the block-tin tube of the condenser. In each distillation, after the first 4 litres had been rejected, the water was collected and stored in a Jena-glass stoppered bottle of 15 litres capacity. Each lot of water was tested in the nephelometer, and found to be free from chlorine; it was used without undue delay.

Nitric Acid.—The purest commercial nitric acid was twice distilled in an apparatus constructed entirely of glass, and in each distillation the first third which passed over and a small endfraction were rejected. A careful nephelometric test for chlorine on the diluted acid gave negative results; the amount of chlorine present in any quantity of acid used in the subsequent work must therefore have been negligible.

For use in the preparation of silver the acid was further redistilled from a still of about 1000 c.c. capacity; the still, still-head, condenser, adapter, and receiver being constructed entirely of platinum.

Ammonia.—For the purpose of these determinations it was obviously unnecessary to free the ammonia from traces of volatile organic bases. The purest ammonia of commerce (D 0.880) was slowly heated in a large Jena-glass flask, and the gas evolved was led through a long, wide Jena-glass tube, suitably bent twice at right angles, directly into pure water contained in a second Jena-glass flask. The joint with the distilling flask was made with tin-foil.

The solution of ammonia thus produced, when acidified with pure nitric acid and tested with silver nitrate in the nephelometer, gave an opalescence which was only just noticeable by comparison with pure water containing no silver; it must therefore have contained a totally insignificant amount of chlorine.

Zinc.—The zinc used in the work was granulated electrolytic zinc, kindly presented by Messrs. Brunner Mond & Co., Ltd. It was used without further purification.

Hydrochloric Acid.—This acid, which was required in the preparation of pure hydrogen, was made according to the method of Thorne and Jeffers (Analyst, 1906, **31**, 101) by digesting the purest commercial acid with a copper-tin couple and then distilling it in an apparatus constructed entirely of glass, a little copper-tin couple and fine copper gauze being placed in the distilling flask. Hydrogen.—This gas, required for use during the fusion of the silver, was prepared by the action of diluted hydrochloric acid on zinc in a Kipp's apparatus. A small quantity of platinic chloride was added to assist the action.

The gas was passed through a special purifying train, the separate parts of which were fused together, and comprised a sloping tube 30 cm. long containing 50 per cent. potassium hydroxide solution, 60 cm. length of tube containing lumps of fused potassium hydroxide, and 30 cm. length of tube filled with phosphoric oxide. The two rubber joints used to connect the purifier with the Kipp's apparatus and the electric furnace were of the best black rubber tubing, within which the ends of the glass tubes met.

The hydrogen issuing from the purifiers was of a high order of purity, as in a Marsh test, in which about 20 litres of gas passed, no visible deposit was formed on the capillary. About 12 litres of the gas were burnt in a current of purified air, and the water produced tested for carbon dioxide with dilute barium hydroxide. Only the faintest turbidity was produced. Hence the hydrogen was free from hydrocarbons.

Chlorine.—The chlorine used in the preparation of the vanadyl trichloride was taken from a steel cylinder of the liquefied gas prepared at the Stassfurt Alkali Works by the electrolysis of brine.

Vanadyl Trichloride.--Vanadyl trichloride was prepared from various samples of vanadic acid by the classic method of Berzelius. About 50 grams of vanadium pentoxide were introduced into a Jenaglass tube drawn out at the end into a "goose neck." Hydrogen was generated by the action of sulphuric acid containing a little copper sulphate on granulated zinc, and passed successively through (i) a solution of lead oxide in aqueous sodium hydroxide solution, (ii) an aqueous solution of silver nitrate, and (iii) concentrated sulphuric acid. The tube was heated to dull redness while a current of this hydrogen was passed through, and the reduction was carried on until no more water appeared to be formed; the vanadium trioxide was allowed to cool in hydrogen. From certain samples of vanadium pentoxide a little metallic arsenic was evolved and condensed near the open end of the tube; in all such cases the arsenic was completely driven out of the tube by heating the end with a free flame.

The vanadium sesquioxide was treated with chlorine at a dull red heat, a bulb trapped with a U-tube containing concentrated sulphuric acid and cooled with ice, being used for the collection of the vanadyl trichloride. The connexion between the receiver and the tube was made gas-tight by means of a wrapping of pure leadfoil coated externally with Chatterton cement. The product was preserved in stoppered bottles. The action proceeds as indicated in the equations:

$$V_2O_5 + 2H_2 \longrightarrow V_2O_3 + 2H_2O,$$

$$3V_2O_3 + 3Cl_2 \longrightarrow 2VOCl_3 + V_2O_5$$

The yield generally obtained was about 95 per cent. of the calculated. The vanadium pentoxide regenerated in the process was set aside and worked up later.

As starting material five samples of vanadium pentoxide and one sample of vanadium sesquioxide were employed.

Sample 1, vanadium pentoxide (98 per cent.) from Pittsburg.

Sample 2, pure oxide, prepared by Sir Henry Roscoe.

Sample 3, oxide from Mottram.

Sample 4, pentoxide obtained at Pittsburg by calcination of a solution of the sesquioxide in oxalic acid.

Sample 5, rich oxide ore from Pittsburg.

Sample 6, pure sesquioxide prepared by Sir Henry Roscoe.

From these samples 1400 grams of vanadyl trichloride were prepared, some of which was yellow and some brown, probably owing to the presence of vanadium tetrachloride.

Each lot of crude material was then distilled, the main fractions boiling between 126° and $127^{\circ}/760$ mm., being kept separately and the first and last fractions rejected. These distillations were carried out in an apparatus constructed entirely of glass, the thermometer being fixed by a joint of fused silver chloride into the ground-glass stopper of the flask. The six main fractions were united in pairs, boiled for six hours with metallic sodium in a glass apparatus, and again distilled, the three main fractions being collected and the first and last fractions mixed with those from the first distillations. The main fractions were united, again heated with sodium for six hours in the glass reflux apparatus, and distilled. The first and last fractions were again rejected, and two main fractions collected: (I) of 420 grams, (II) of 240 grams.

Fraction II was decomposed by water and converted into vanadium pentoxide by repeated evaporation with nitric acid. The product was extracted six times with small quantities of water, and the washings divided into two parts, which were tested respectively (a) for arsenic, by Marsh's test, (b) for phosphoric acid by means of ammonium molybdate. No trace either of arsenic or phosphorus was detected.

Fraction I was further redistilled, rejecting the first and last fractions, the main fraction being preserved in a sealed glass vessel until required for use.

From observations made during these distillations it was convol. CV. 4 R

cluded that the boiling point of pure vanadyl trichloride at 760 mm. approximates closely to 127°.*

Silver.—Three samples of silver were prepared.

Sample 1 was prepared by a modification of the well-known bisulphite method of Stas. A cold dilute solution of commercial silver nitrate was treated with a slight excess of the purest hydrochloric acid of commerce, the precipitate repeatedly washed by decantation with cold water, digested with nitric acid for about eight hours at 100° in a platinum dish, and again washed thoroughly with water. The silver chloride was then covered with water in a large Jena-glass bottle, and ammonia gas was passed into the liquid until complete solution of the silver chloride was effected. For each 10 grams of silver present 1 gram of electrolytic copper was weighed out. The copper was first cleaned with nitric acid, washed with water, dissolved in a slight excess of nitric acid, and the solution added to the ammoniacal silver solution, and more ammonia passed into the mixture. The silver was then precipitated in a crystalline form by diluting with water until there was 50 c.c. of solution present for every gram of silver, adding an excess of ammonium bisulphite solution, and warming to about 80°. The bisulphite was prepared by leading into water ammonia and sulphur dioxide, the latter from the middle fraction of the liquid in an ordinary syphon. The precipitated silver was repeatedly digested with concentrated ammonia, and washed by decantation with water. It was then dried at 250° in a small electric oven, constructed from a Jena-glass beaker by winding it with nichrome ribbon and packing it with magnesia inside a larger beaker.

Sample 2 was prepared by the formate method. Silver nitrate was twice recrystallised, once from nitric acid (D 1.2) and once from water. In each case the crystals were centrifugally drained to remove the mother liquor, and washed with a little water. The salt was then dissolved in water, and reduced by means of ammonium formate. The water, ammonia, and formic acid were prepared immediately before use, the last-named by redistilling Kahlbaum's purest formic acid in the platinum still previously mentioned, and rejecting the first runnings. The preparation was carried out, as described by Richards and Wells (J. Amer. Chem. Soc., 1905, 27, 459), in vessels of Jena glass, and the resulting silver washed, first with ammonia and then with water, and dried at 250° .

Sample 3 was prepared from the greater part of sample 1 by

^{*} The preparation of the vanadyl chloride thus far, and the tests above described, were carried out by one of us under the direction of Sir Edward Thorpe, to whom our thanks are due for the gift of this material.

dissolving it in a slight excess of nitric acid, neutralising the solution with ammonia, and then reducing it with ammonium formate, as in the case of sample 2. The silver was washed and dried as before.

Before any sample of silver was weighed out for use in analysis it was fused in a current of hydrogen, cooled in hydrogen, thoroughly etched with nitric acid, washed successively with water, ammonia, and water, dried at 250°, and cooled in a desiccator over potassium hydroxide. As a support for the silver during the fusion, boats of fused quartz, lime, and magnesia were tried. The first-named cannot be recommended as they crack after one or two fusions have been made, and the lime boats could not easily be prepared of the requisite strength, at least by the method of Richards and Wells. Magnesia boats of a fair degree of strength are, however, readily constructed, and serve admirably as supports for the silver. Considerable difficulty was at first experienced in obtaining magnesia free from sulphur, but a sample containing only a trace of sulphur was eventually prepared by igniting in an electrically-heated muffle furnace * basic magnesium carbonate obtained from the purest commercial magnesium nitrate by repeated precipitation with pure sodium carbonate. This magnesia was moulded with water into the proper shape, dried, and the last trace of sulphur was then readily eliminated by heating the boat to 1000° for three hours in a current of moist pure hydrogen.

The furnace used in this operation and in the fusion of the silver was made by winding the central 25 cm. of a porcelain tube (60 cm. by 3.5 cm.) with 9.6 metres of nichrome ribbon (0.16 cm. by 0.036 cm., or $1/16'' \times 0.0142''$), and insulating it with a layer of asbestos 8 cm. thick. The current was taken directly from the lighting circuit (105 volts), and a temperature of 1100° was readily obtained.

An assortment of very small pieces of silver being required for adjusting the weight of silver in each experiment as exactly as possible, a large button of silver (sample 1) was drawn into a number of wires of different thicknesses, the wires being repeatedly etched during the drawing to remove any iron from their surfaces. They were then cut by means of a clean chisel into pieces varying in length from 1 to 4 mm., the whole etched with nitric acid, washed, and dried at 250° .

From a consideration of the work of Stas, Richards, Scott, and

* This furnace was constructed by winding 11.3 metres of No. 17 Brown and Sharpe nichrome wire on a clay \Box -section muffle 14 cm. wide; the winding was covered with a paste of magnesia and water and dried slowly, and the whole packed with slag-wool in a uralite box. With a current of 9 amperes at 105 volts it attained a steady temperature of 1000° in an hour.

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others it is evident that the silver used in this investigation was of a high order of purity. In the cases of samples 1 and 3 this conclusion is, further, supported by the results of a series of comparative assays made at the Royal Mint, for which purpose buttons of these samples were submitted. After numerous preliminary assays they were compared with the best sample of proof silver. Taking the latter as 1000 fine, the results were as follows:

 Sample I.
 999.97 fine.

 Sample III.
 999.98 fine.

These results were each the mean of three concordant determinations.

The authors are indebted to Messrs. S. W. Smith, B.Sc., A.R.S.M., and W. A. C. Newman, B.Sc., A.R.S.M., Assistant Assayers of the Royal Mint, for their kindness in carrying out these comparative assays.

The Determination of Weight.

Every care was taken to make the error in weighing so small as to be insignificant in comparison with the other possible errors of experiment. Accordingly, the vanadyl trichloride and silver were weighed on a long-beam Oertling balance, sensitive to the hundredth of a milligram. The sensitiveness of this balance increased with the load; throughout most of the work it was 50 scale divisions per milligram with a load of 10 grams in each pan. The smallest weight used was the 5-milligram weight, the rider also weighing 5 milligrams.

In the process of weighing, the rider was adjusted to within 1/10th of a milligram of the correct value, and the fifth decimal determined by the method of oscillations. All weighings were made directly, there being no necessity to resort either to the method of substitution or to the method of reversals, since interchanging the object and the weights produced no change in the fifth decimal place with the loads employed. The zero of the balance was always taken before and after each weighing, and whenever necessary the object weighed was balanced against a tare resembling it as nearly as possible in material, shape, volume, and weight. The balance-room had a northern aspect, and the temperature variation did not exceed 3° throughout the entire investigation. The levelling screws of the balance stood on three glass plates, which in turn rested on three packets of filter paper, the whole being supported on a stone slab let into the wall. All weighings were made as late in the evening as possible, usually

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after 10 p.m., to minimise the disturbances due to passing traffic, etc.

The weights used were carefully compared among themselves, and from the observations their relative values in air were deduced. All weights given in this paper represent relative weights in a vacuum. The vacuum correction to be applied to the weight of an object consists of two parts, one positive and equal to the weight of air displaced by the object, and the other negative and equal to the weight of air displaced by the weights used. Provided that the relative values of the weights in air are known, this second correction is obviously unnecessary. It was accordingly omitted, and the following vacuum corrections applied:

From the manner in which the glass bulbs containing the vanadyl trichloride were prepared (p. 1326), it will be seen that the only correction necessary to the apparent weight of the liquid was the weight of air contained in the bulb at the time it was initially weighed.* The determination of this correction necessitated a knowledge of the temperature and pressure of the atmosphere at the time the bulb was first weighed and of the internal volume of the bulb. The latter was obtained by calculation from (i) the weight of glass in the bulb, and (ii) its external volume as determined by weighing it in air and in water. An example of the method of calculation is given on p. 1330.

Owing to the large weight of the Gooch crucibles employed, the weights of the silver chloride precipitates produced in the gravimetric experiments were determined by the method of reversals on a small Sartorius balance. They are probably accurate to 1/20th milligram. In determining the corrections rendered necessary by loss of asbestos and retention of water, the Oertling balance was used.

The air in the balance case was kept dry by means of potassium hydroxide.

The Nephelometer.

In the determination of the quantity of silver equivalent to a known amount of vanadyl trichloride, use was made of a nephelometer rather simpler in construction than that used by Richards and Wells (*Amer. Chem. J.*, 1904, **31**, 235). The main constructional details are indicated in Fig. 1, T_1 and T_2 being the test-tubes

^{*} Not the weight of air which would have filled the bulb at the time it was weighed filled with liquid, because the bulb and stem in each case (p. 1328) were balanced against a similar tare in which the capillary between the bulb and stem had been closed by fusion.

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in which the turbidities to be compared are produced, D_1 and D_2 are the dark sliding tubes by means of which the lengths of turbid liquid exposed to light are varied, and M_1 and M_2 two parallel plane mirrors inclined at 45° to the axes of the tubes. The front mirror is so adjusted as to cover only half the front tube, so that, on looking through O, the circle of view comprises in one-half the image of half the back tube, and in the other half that of half the front tube. The mirrors used were cut from the same piece of glass, and silvered in the same silvering bath. Experiment proved that the measurement of the ratio of the turbidities produced in two tubes was unchanged when the positions of the tubes were reversed.

In carrying out nephelometric tests all the precautions mentioned by Richards and Wells (J. Amer. Chem. Soc., 1905, 27, 459) were



taken. The test-tubes were made in pairs from the same piece of tube, and each pair similarly etched; the open ends of these tubes were ground flat, and their contents were protected from the atmosphere by plane glass covers.

After a short experience of the process all measurements were carried out in duplicate, 100 c.c. of liquid being withdrawn and 25 c.c. run into each of four tubes. To one tube of each pair was added 1 c.c. of a solution of silver nitrate containing 1 mg. of silver per c.c., and to the other 1 c.c. of an equivalent solution of sodium chloride. When two turbidities thus produced are equal in intensity, it is clear that the concentrations of silver and chlorine in the liquid are equivalent, and hence are to be attributed solely to the dissolved silver chloride; in other words, the end-point has been reached in the titration.

Final Purification of Vanadyl Trichloride and its Collection for Analysis.

The principal departure from previous practice was made in the fractional distillation of the vanadyl trichloride and its collection The method adopted by Prandtl and Bleyer for this in bulbs. part of the determination appears to be unsatisfactory. The liquid was introduced into their apparatus by pouring-a procedure which must have involved contact with air-and then twice distilled without exposure to air, rejecting the last fraction in each distillation. The final fraction was collected in a conical flask into the bottom of which a number of fine tubes carrying the bulbs were inserted. It is obvious from the manner of filling the bulbs that no sharp separation into fractions could have been attained. \mathbf{It} would also appear that the different parts of the apparatus were connected together by rubber stoppers, a plan which is to be deprecated in the case of a liquid having the properties of vanadyl trichloride.

In designing a distillation apparatus the authors endeavoured to fulfil the conditions (1) that the fractionation should be carried out without any exposure to atmospheric moisture, (2) that taps should, as far as possible, be avoided, and (3) that the method of weighing should not involve the difficult process of collecting and weighing the fragments of a broken bulb. After numerous attempts the apparatus described below was devised, and was found to be thoroughly satisfactory. The construction of this apparatus was only rendered possible after a special type of joint had been devised; this will be described at this point, and in some detail, because it is readily constructed, appears to be capable of wide application, and apparently has not been described previously.

The Special Joint.—This joint is represented diagrammatically in Fig. 2. A wide tube A has sealed into one end of it the tube B, the narrow part of which lies inside A; the narrow tube is left open at C, and has a scratch round it at D. Afterwards the wide tube is drawn down and sealed to the tube E, and the open sidetube F is inserted. In this condition the whole is sealed at the end B into the vessel V, from which the distillation is to take place in such a way that the side-tude is horizontal when V is in its normal position. The whole apparatus is then cleaned with chromic and nitric acids, washed, and dried by means of a current of dry air. At this stage the narrow tube is sealed at C by means of a minute gas flame burning at a platinum jet on the end of a long capillary Jena-glass tube, which is introduced through the tube E; this flame is fed by oxygen led in through the side-tube F. The sealing of C takes place almost instantaneously, and no appreciable amount of moisture is introduced into the tube B.

The vessel V may now be used for the reception of any material desired, and then sealed off at G. In this condition it is hermetically sealed, and its contents may be kept unchanged indefinitely.

For the purpose of distilling the liquid into another vessel the latter is sealed on to the tube E, and is cleaned, washed, and dried together with the body of the joint. Then a piece of glass rod of such a size as will slide easily in F is introduced therein, and the open end of the side-tube is sealed off. The new vessel and the open part of the joint may now be exhausted and sealed off from the pump, and connexion established between it and the first vessel V by inclining the apparatus so that the glass rod falls down the side-tube and knocks off the end of the narrow tube CD.

It will be seen that the joint, in effect, serves as a tap which can



be opened once and closed once (by sealing off at B or E), without any possibility of leakage and without bringing the contained material into contact with anything other than dry glass.

Outline of Method of Purification.—The final purification of the vanadyl trichloride consisted in digesting with metallic sodium a portion of fraction I (p. 1317), and separating this by distillation in a vacuum into four main fractions, A, B, C, and D, smaller fractions at the beginning and end being rejected. Fraction A was then further fractionated into six parts, of which the first and last were rejected, and fractions 2 to 5 collected in weighed bulbs. This was done chiefly for the sake of practice in the method, as the material was slightly brown, and the bulbs were used only for preliminary determinations.

The main fractions, C and D, were redistilled into eight and ten fractions respectively, the middle 6 and 8 respectively being collected in bulbs for use in the determinations.

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THE ATOMIC WEIGHT OF VANADIUM.

Digestion with Sodium and First Fractionation.—About 2 grams of clean metallic sodium, cut from the middle of fresh lumps of the metal, were placed in a 150 c.c. flask F (Fig. 3) having a long neck, into which were sealed a special joint E and a U-tube G. The neck was then constricted at H, 105 grams of vanadyl trichloride were poured in through a long funnel, and the neck was sealed off at H. The flask was then heated on a sand-bath, and its contents were gently boiled for twelve hours, and finally the U-tube was sealed off at J. An apparatus of the form shown in the figure was then sealed on to the flask at K. The vessels A, B, C, D, intended for the reception of the main fractions, each carried a special joint, the narrow tubes in these joints being left open



until the whole apparatus had been carefully cleaned and dried by a current of dry air which passed in at L and out at M and N. Next, the glass rod was introduced into the side-tube at M, and the side-tube sealed up; the bulb at N was also sealed. The apparatus was connected with a Gaede pump through a long tube containing phosphoric oxide and exhausted, being heated cautiously the while by a free flame. Air was then re-admitted slowly to the apparatus, and the whole exhausted as before. This procedure was repeated four times in order to free the apparatus from any possible trace of water. Then the flask was cooled in a freezing mixture of ice and crystallised calcium chloride, the joint E was broken, and the pump was kept working until vanadyl trichloride began to condense in the catch-bulb O, which was cooled in liquid air; lastly, the apparatus was sealed off from the pump at P.

A small fraction was first distilled into the bulb R by warming F cautiously in a current of warm air from a burner and cooling R in liquid air; then, whilst the bulb was still kept cool, the capillary at S was sealed. By a similar method each of the tubes A, B, C, D in succession was about half-filled with distillate and sealed off from the rest of the apparatus. The end-fraction was left in the flask.

Final Fractionation into Bulbs.—The further fractionation of the distillate was effected in the following manner: The special joint of the tube containing the main fraction was fused on to a straight tube carrying a series of ground sockets in the manner indicated in Fig. 4. The bulbs, of the form shown at A, were attached to tubes ground into these sockets, corresponding tubes and sockets being similarly numbered by etching. These tubes and sockets were very carefully made from flawless tube, and were finally polished with rouge and turpentine. They would hold a moderate vacuum without any lubricant.

After the apparatus had been very carefully cleaned and dried and the bulbs had been weighed, the latter were fitted to their sockets, a very small quantity of grease, compounded of unvulcanised rubber, paraffin, and vaselin, being smeared on the upper half only of the joints. As the lower parts of the joints fitted excellently, the vanadyl trichloride vapour did not come into contact with the grease.

When the bulbs had been fitted, the glass rod was introduced into the joint, and the side-tube and the capillary N were sealed up. The apparatus was then connected through the bulb O and a phosphoric oxide tube with the Gaede pump, exhausted, and sealed off from the pump at P.

The joint was broken by tilting the apparatus, and a first fraction was distilled into the bulb R, which was sealed off whilst still immersed in liquid air. Subsequently the bulbs were filled and sealed off one by one.

During the distillation the apparatus was kept at about 25° by a current of warm air rising from resistance coils, and the vapour was caused to condense in any desired bulb by immersing it in liquid air. Each bulb was sealed off at the capillary as rapidly as possible immediately after it was filled, and preserved in a numbered box.

In no case was the slightest sign of any decomposition of the vanadyl trichloride observed during the sealing.

In connexion with this part of the distillation a curious point

arose. It was found that when a bulb was first cooled a considerable condensation of vanadyl trichloride took place, and it became about one-third filled in two to three minutes, after which continued cooling even for three hours caused no great increase in the amount of material condensed. It seemed possible that this might be due to the fact that a certain amount of air must have been left in the apparatus (although its pressure was certainly less than $\frac{1}{2}$ mm.). The following sequence of events may then be imagined: The bulb is cooled, and a quantity of vanadyl chloride vapour and air rushes in; the vanadyl chloride is condensed (its vapour pressure may be taken to be negligible at the temperature of liquid air), whilst the air remains as gas. This goes on until the bulb contains only solid vanadyl trichloride and air, the latter at a pressure equal to the combined pressures of vanadyl chloride



vapour and air in the rest of the apparatus. When this point is reached the vapour of the chloride can only reach the bulb by the slow process of diffusion along the stem and through the capillary.

If this hypothesis is correct it should be easy to fill the bulb by alternate heating and cooling, just as a thermometer is filled. This procedure was accordingly tried, and found to answer satisfactorily; by surrounding the bulb alternately with liquid air and with alcohol at room temperature it was possible to fill it completely in about ten minutes.

Methods of Analysis.

In each experiment the bulb containing the vanadyl trichloride was cleaned externally and dried over sulphuric acid. The stem corresponding with the bulb was also dried, and the bulb, liquid, and stem were then weighed together after remaining in the

BRISCOE AND LITTLE :

balance case for at least twelve hours. The bulb was lowered, by means of a long glass rod drawn out to a hook at the end, into a strong resistance glass bottle of 2 to 5 litres capacity. A slight excess of an aqueous solution of ammonia was introduced into the bottle, the stopper securely tied in, and the whole cooled to 0° . By shaking the bottle the small bulb was then broken.

After it had remained for at least twenty-four hours, the bottle was again cooled to diminish the internal pressure, the stopper was removed and rinsed into the bottle, and the liquid diluted with ice-cold water to at least 700 c.c. Any large fragments of the bulb were broken up by means of a stout glass rod.

In the determination of the ratio VOCl_3 : 3Ag, from 45 to 50 c.c. of concentrated nitric acid were measured out, diluted to 300-400 c.c. with water, cooled to 0°, and then carefully poured into the cold slightly ammoniacal solution contained in the bottle, the whole being mixed by careful shaking.

Meanwhile, a button of silver, slightly less in weight than that actually required to react with the chloride, was prepared in the manner already described (p. 1319). By the addition of one or two small pieces of silver wire the quantity of silver was brought to within 2 or 3 milligrams of the correct amount; its weight was then accurately determined. This silver was dissolved in 45 c.c. of nitric acid diluted with its own volume of water. The solution was effected in a 1000 c.c. Jena-glass flask fitted with a groundglass stopper carrying a set of splash-bulbs, which was gently heated over a nichrome resistance board; a test experiment showed that no silver was splashed up into the bulbs. This solution was diluted to 300—400 c.c., and gently boiled to expel nitrous acid; it was then allowed to cool, and diluted to at least 800 c.c. with water.

As soon as the solution of ammonium chloride and vanadate had been acidified, the solution of silver nitrate was slowly added to it, the whole being kept in a state of gentle agitation throughout the process. The flask containing the silver solution was then thoroughly rinsed with water, and the rinsings were poured into the precipitation bottle.

The estimated deficit of silver (2 or 3 milligrams) was made up by the addition of the required amount of a dilute standard solution of silver nitrate. The whole was gently shaken and allowed to remain with occasional gentle agitation for one or two days.

One hundred c.c. of the supernatant liquid was then examined nephelometrically (p. 1321) to see whether the concentrations of silver and chlorine in it were equivalent, in which case the experiment would have been at an end. Usually it was found that the concentration of the silver was too small. From the ratio of the concentrations and an approximate knowledge of the solubility of silver chloride in the supernatant liquid, the deficiency of silver (or chlorine) was estimated by a simple application of the principle of the solubility product. This deficit was then supplied by means of a very dilute solution of silver nitrate (or sodium chloride), the whole vigorously shaken, allowed to remain at least twenty-four hours, and the nephelometric test again made. Further addition of silver nitrate or sodium chloride was made if necessary, and in this manner the end-point in the titration was eventually reached.

In each experiment the precipitation of the silver chloride was carried out in a room lighted only by means of a red light. Except when liquid was to be withdrawn, the bottle was kept in a dark cupboard, the temperature of which was 10°. In the later stages of the titrations the bottles were occasionally exposed to the light from an ordinary filament lamp for short periods, a procedure which had no deleterious effect upon the precipitate, since the supernatant liquids were, with one exception, yellow. In the analysis of fraction D2, however, the nitrous acid was not boiled out of the silver nitrate solution, and the liquid was accordingly blue owing to reduction of vanadic acid to a vanadyl salt. In order to maintain the atmosphere of the room free from chlorides, the only hydrochloric acid ever brought into it was that contained in the Kipp's apparatus, which was filled outside and trapped with strong potassium hydroxide solution, and the analyses were conducted at a time when the contamination of the air of the adjoining laboratory was at a minimum.

In the two determinations of the ratio $VOCl_3$: 3AgCl the ammoniacal chloride solutions were filtered from the fragments of glass before they were acidified with nitric acid. The precipitation was conducted in a 4-litre Erlenmeyer flask fitted with a groundglass stopper. The precipitates were collected on asbestos in porcelain Gooch crucibles, and their weights corrected for (a) air displaced, (b) asbestos lost during filtration and washing, (c) silver chloride dissolved in the filtrate and washings, and in the **ammonia**cal rinsings of the precipitation flask, and (d) water retained by the precipitate at 250°. The procedure described by Richards and Willard (J. Amer. Chem. Soc., 1910, **32**, 4) in their analyses of lithium chloride was closely followed in these two analyses.

Results.

In all, nine determinations of the ratio $VOCl_3 : 3Ag$ and two of the ratio $VOCl_3 : 2AgCl$ were effected. Two experiments, namely, those dealing with fractions C1 and D4 met with accidents, and

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were not completed. No attempt was made to analyse fraction D 3, since the hook snapped from the vanadyl trichloride bulb before the weighings were commenced.*

For the sake of illustrating the foregoing description of the experimental method employed, the data relating to the analysis of fraction C 2 are set out in detail below:

Analysis of Fraction C2.

1. Bulb and stem ; excess weight over tare *	(a) Weight of Vanadyl Trichloride :	
* $t=16\cdot5^\circ$; $p=768\cdot0$ nm. (corr.). 3. Bulb and VOCl ₃ ; weight in air	 Bulb and stem; excess weight over tare* Bulb, VOCl₃ and stem; excess over tare	$0.31145 \\ 4.28985 \\ 3.97840$
3. Bulb and VOCl ₃ ; weight in air	* $t = 16.5^{\circ}$; $p = 768.0$ mm. (corr.).	
 4. Bulb and VOCl₃; weight in water	3. Bulb and VOCl ₃ ; weight in air Weight of glass bulb $(1+3-2)$ And Volume of glass of bulb $(D \ 2.50) = 0.8198 \times 0.4$ = 0.328 c.c.	4·7982 0·8198
 l c.c. dry air at 16.5° and 768 mm. weighs 1.228 mg. ∴ Vacuum correction=1.228×2.624 mg.=3.22 mg. And corrected weight of VOCl₃=3.97840+0.00322 =3.98162 grams. (b) Weight of Silver : (i) Crucible+silver; excess over tare	 4. Bulb and VOCl₃; weight in water ∴ Loss of weight in water (3-4) Hence, with sufficient accuracy, external volume of bulb=2.952 c.c., and internal volume of bulb=2.952 →0.328=2.624 c.c. 	$1.846 \\ 2.952$
 (b) Weight of Silver : (i) Crucible+silver; excess over tare	l c.c. dry air at $16\cdot5^{\circ}$ and 768 mm. weighs $1\cdot228$ mg. \therefore Vacuum correction = $1\cdot228 \times 2\cdot624$ mg. = $3\cdot22$ mg. And corrected weight of $VOCl_3 = 3\cdot97840 + 0\cdot00322$ $= 3\cdot98162$ grams.	
 (i) Crucible+silver; excess over tare	(b) Weight of Silver :	
 ∴ Weight of silver in air 7.43 Vacuum correction (7.43 × 0.117 mg.)	(i) Crucible+silver; excess over tare	$7.71486 \\ 0.28519$
 Weight of silver in vacuum	Weight of silver in air Vacuum correction (7.43 \times 0.117 mg.)	7·42967 0·00087
 (ii) Silver nitrate solution was prepared containing 0.204 mg. of Ag per c.c. Added 19.0 c.c. = 0.00 (iii) Nephelometric test on 100 c.c. liquid : Equiv. conc. Ag : ditto of Cl::95:100. Hence, added 0.50 c.c. silver nitrate solution	Weight of silver in vacuum	7.43054
 (iii) Nephelometric test on 100 c.c. liquid: Equiv. conc. Ag : ditto of Cl::95:100. Hence, added 0.50 c.c. silver nitrate solution	(ii) Silver nitrate solution was prepared containing 0.204 mg. of Ag per c.c. Added 19.0 c.c.=	0.00387
seven days.	 (iii) Nephelometric test on 100 c.c. liquid: Equiv. conc. Ag : ditto of Cl:: 95:100. Hence, added 0.50 c.c. silver nitrate solution Nephelometric test on 100 c.c. liquid : Equiv. conc. Ag : ditto of Cl:: 100: 99. This was accepted as the end-point. Volume of liquid = 2 litres; hence correction for first 100 c.c. removed is negligible. Duration of analysis, seven days. 	0.00010
Hence, total silver used = 7.4	Hence, total silver used =	7.43451

^{*} In connexion with this bulb a curious fact, hitherto unrecorded was observed. It was left exposed to light in the balance case for some months and during this time the contents became noticeably brown. It seems possible that this change may be due to the decomposition of $VOCl_3$ into $VOCl_2$ and chlorine.

Atomic weight of

Atomic weight of

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Analysis of Fraction C2 (continued).

(c) Result :

 $\begin{array}{l} {\rm VOCl}_3: 3{\rm Ag}:: 3\cdot98162: 7\cdot43451 \\ i.e. :: 173\cdot328: 323\cdot640 \ (i.e., \ 3\times107\cdot880). \\ {\rm Hence, \ molecular \ weight \ of \ VOCl}_3=173\cdot328, \\ {\rm And} \quad {\rm atomic \ weight \ of \ vanadium}=50\cdot948 \ (Cl=35\cdot460) \\ =50\cdot957 \ (Cl=35\cdot457). \end{array}$

In tables I and II the final results of all the experiments are tabulated.

Dealing with the results contained in table I it will be seen that the nine values for the ratio $VOCl_3$: 3Ag range from 0.53547 to 0.53557, an extreme variation of 1 part in 5355. Two of the results, however, namely, Nos. 3 and 9, merit less confidence than the others, since they differ from the mean by 0.00006 and 0.00007 respectively, whilst in no other case does the deviation exceed 0.00003. Since the deviations in these two experiment are in the

TABLE I.

 $VOCl_3 : 3Ag.$

						vana	dium.
	Fraction	Weight of	Sample	Weight of			<u> </u>
	\mathbf{of}	VOCl ₃	of	Ag in		Cl =	Cl =
Тo.	VOCl ₃ .	in vacuum.	silver.	vacuum.	VOCl ₃ /3Ag.	35.460.	35.457.
1	C 2	3.98162	II	7.43451	0.53556	50.948	50.957
2	C 3	5.63804	1	10.52736	0.53556	50.949	50.958
3	C 5	3.70889	1	6.92632	0.53548	50.922	50.931
4	C 6	3.88228	II	7.24884	0.53557	50.953	50.962
5	D 1	$3 \cdot 28485$	III	6.13377	0.53554	50.941	50.950
6	D 2	$3 \cdot 45920$	III	6.45900	0.53556	50.950	50.959
7	D 5	3.17088	II	5.92089	0.53554	50.942	50.951
8	D 6	3.63990	III	6.79670	0.53554	50.942	50.951
9	D 7	3.32354	11	6.20682	0.53547	50.918	50.927
	34				0 59554	50.041	50 050
	Mean				0.53554	50.941	20.920
	Mean, rej	jecting 3 and	£ 9		0.53555	50.946	50.955
	Mean of I	Fraction C .			0.53554	50.943	50.952
	Mean of 1	Fraction D			0.53553	50.939	50.948
	Mean of I	Fraction C_{1}	rejecting	3	0.53556	50.950	50.959
	Mean of 2	Fraction D ,	rejecting	, g 9	0.53555	50.944	50.953
			- 1				

TABLE II.

$VOCl_3 : 3AgCl.$

vanadium. Fraction Weight of Weight of Cl =Cl== VOCl₃ of AgCl No. VOCl₃. in vacuum. in vacuum. VOCl₃/3AgCl. 35.460. 35.457. C 4 4.4227910.9718750.96250.968 0.403101 $\mathbf{2}$ D 82.625576.514590.4030350.93150.936Mean..... 0.4030750.94750.952

N

direction to be anticipated from a consideration of the possible experimental errors, it seems reasonable to omit these two results in taking the final mean. The mean of the remaining seven values is 0.53555, with a probable error of only 3.3×10^{-6} , the individual values varying from 0.53554 to 0.53557, that is, by approximately 1 in 18,000. The probable error of the mean of all the nine values is 8.2×10^{-6} .

The close agreement of experiments 1 and 4, in which the same sample of silver (II) was used, shows that the fractionation of fraction C of vanadyl chloride had no effect on its composition. A similar conclusion concerning fraction D may be inferred from the close agreement of experiments 5 and 8, in each of which sample III of silver was used. The excellent concordance of seven of the nine results indicates that the three samples of silver were of the same degree of purity, and hence justifies the conclusion that fractions C and D of vanadyl chloride were essentially identical in composition. It is therefore reasonably certain that the vanadyl chloride analysed must have been free from any significant amount of impurity.

The possible sources of error in the determination of the ratio $VOCl_3$: 3Ag are as follows: (1) presence of chloride in the reagents used (water, ammonia, nitric acid), and in the atmosphere; (2) mechanical loss of silver nitrate when transferring the solution to the precipitation bottle; (3) impurity in the silver used; (4) occlusion of soluble chloride by the precipitated silver chloride; (5) co-precipitation of silver vanadate with the silver chloride. The atomic weight deduced would be greater than the true value, owing to error (4) and less owing to errors (1), (2), (3), and (5). The error due to (1) may doubtless be neglected in view of the extreme care taken in testing the reagents, and in maintaining the air of the laboratory free from hydrochloric acid. That due to (2) cannot very well be estimated. The transference of the silver nitrate solution was effected with great care, and in no case was there any suspicion of loss at the time of transference. The error due to (3) must be very small, and the uncertainty it introduces into the atomic weight of vanadium is certainly less than 1 unit in the second decimal. That due to (4) can only be at the maximum 1 part in 35,000, if it is legitimate to compare the analyses recorded in table I with Baxter and Moore's analyses of phosphorus trichloride (J. Amer. Chem. Soc., 1912, 34, 1644). The actual error introduced, however, can only be a fraction of this maximum value since in seven of the nine titrations the end-point was only reached after the lapse of a fortnight or more, and, according to the experiments of Baxter and Moore, end-points so determined very seldom alter on further keeping. Moreover, the ratio $VOCl_3 : 3Ag$ was found to be practically independent of the final volume of the mixed solutions, which, for example, amounted to 4 litres in experiment 5 and 2 litres in experiment 8. The error due to (5) must also have been extremely small. In only one experiment was the silver chloride obviously contaminated with silver vanadate. This was due to an oversight, the silver nitrate solution not having been acidified sufficiently with nitric acid, and the experiment (on fraction C1) was rejected. That the precipitated silver chloride cannot have been contaminated with any noteworthy quantity of impurity is indicated by the fact that in the two gravimetric experiments given in table II the silver chloride fused to an almost perfectly colourless liquid.

The two determinations of the ratio $VOCl_3 : 3AgCl$ call for little comment. They were carried out to afford a check on the gravivolumetric results, in comparison with which they carry little weight. The two experiments are, however, fairly closely concordant, and the mean result is in excellent agreement with the average result of the other series of experiments, an indication of the substantial accuracy of the analytical work.

In seeking to deduce the most probable value for the atomic weight of vanadium from the preceding results it is necessary (1) to bear in mind that the value deduced from the experiments is most likely to err by being a trifle low, and (2) to consider the degree of accuracy of the antecedent data, namely, the atomic weights of silver and chlorine. The latter are given in the International Table as 107.88 and 35.46 respectively, but it is very probable that the numbers 107.880 and 35.457, determined by Richards and his co-workers, represent more closely the ratio of these two atomic weights, whilst a number of recent investigations lead to the conclusion that the value 107.88 for silver is to be regarded as a maximum.

The use of the latter pair of values leads to an atomic weight of vanadium 0.009 or 0.006 in excess of that given by the former pair according as the ratio $VOCl_3$: 3Ag or $VOCl_3$: 3AgCl is considered.

According to the value adopted for the atomic weight of chlorine, the seven closely concordant titrations given in table I lead to the value 50.95 or 50.96 for the atomic weight of vanadium; the two gravimetric results given in table II lead in each case to the rounded off value 50.95. The final result of this investigation may therefore be summed up by stating that the *atomic weight of* vanadium lies between 50.95 and 50.96. The experimental results do not enable a definite decision to be made between these two values; the higher one is perhaps to be preferred.

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This result is in remarkably close agreement with that arrived at by McAdam by the use of a totally different method, and is therefore entitled to be regarded as extremely probable. It is, however, decidedly lower than the results derived from former researches, in which the analytical methods involved were in principle the same as those here described. That there is no inherent improbability attaching to such a low result is readily seen when the extreme values obtained by different experimenters are compared (Cl = 35.457):

Experimenter.	Method.	Atomic weight of vanaduim
Roscoe	Volumetric and gravimetric	50.38 to 52.33
Prandtl and Bleyer.	Gravimetric	50.87 to 51.21
Briscoe and Little.	Volumetric and gravimetric	50.93 to 50.97

Further, it is of interest to note that the extreme values obtained in this investigation differ but slightly from those obtained by McAdam (Cl=35.457):

McAdam.	V lies between	•••••	50.94 and	50.99
Br i scoe and Little	V lies between	•••••	50.93 and	50.97

and that of the eleven values obtained in the course of this work seven lie between the limits 50.950 and 50.962.

The experiments described in this paper, together with those of McAdam, lead to the value 50.96 for the atomic weight of vanadium. To this there appears to be but one objection, namely, the fact that the oxide method has so far yielded a much higher result, but the comparatively small significance attaching to this high result has, however, been already indicated. A re-investigation of the ratio $V_2O_5 : V_2O_3$ is nevertheless desirable. In any such work it would be of interest to determine not only the loss in weight attending the conversion of V_2O_5 to V_2O_3 , but also the weight of water produced in the reaction.

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