only four millionths of a grain is a sufficient proof that the indications of this instrument, like those of the apparatus previously described by the author, follow rigidly the law of inverse squares. An examination of the differences between the separate observations and the mean shows that the author's estimate of the sensitiveness of his balance is not excessive, and that in practice it will safely indicate the millionth of a grain.

One observation of the weight of sunlight is given; it was taken on December 13; but the sun was so obscured by thin clouds and haze that it was only equal to 10·2 candles 6 inches off. Calculating from this datum, it is seen that the pressure of sunshine is 2·3 tons per square mile.

The author promises further observations with this instrument, not only in photometry and in the repulsion caused by radiation, but in other branches of science in which the possession of a balance of such incredible delicacy is likely to furnish valuable results.

February 17, 1876.

Dr. J. DALTON HOOKER, C.B., President, in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read:—

I. "Researches upon the Specific Volumes of Liquids." By T. E. THORPE, Ph.D., F.R.S.E., Professor of Chemistry in the Yorkshire College of Science, Leeds. Communicated by Prof. A. W. WILLIAMSON, For. Sec. R.S. Received January 14, 1876.

II. *On the Specific Volumes of certain similarly constituted Inorganic Chlorides.*

The results of the observations made by Pierre and Kopp upon the boiling-points, specific gravities, and thermal expansibilities of the trichlorides and tribromides of phosphorus, arsenic, and antimony have led Kopp to suppose that the specific volumes of phosphorus, arsenic, and antimony, in their liquid combinations, may be identical. The same conclusion has been drawn with respect to tin, titanium, and silicon from Pierre's observations upon the tetrachlorides of these elements*.

* Ann. der Chem. u. Pharm. xcvi. p. 319. In his original paper Kopp remarks that the specific volume of antimony, from his observations on the chloride, $SbCl_3$, and the bromide, $SbBr_3$, is decidedly larger than that of phosphorus and arsenic. But the larger value is in part due to the atomic weight of antimony being taken as 129. If the more

The common value of P, As, and Sb would appear to be about 27; that of Si, Ti, and Sn about 35. But on examining the details of the observations, it becomes evident that this conclusion is not strictly borne out by the results; the numbers obtained for the individual members of the group differ in many cases considerably from the common value, the divergences being far wider than could arise from errors of observation, either in the determination of the physical constants or in the estimation of the atomic weights of the constituent bodies. In fact the order of the divergences would seem to render it probable that the specific volumes of the several members of a family of elements increase with their atomic weights.

In a former communication to the Royal Society I have given the results of a series of observations on the specific gravities, boiling-points, and rate of expansion of certain liquid chlorides of phosphorus*. Since Roscoe has shown that vanadium is a member of the phosphorus group of elements, it has appeared to me that a comparison of the specific volumes of the analogously constituted phosphoryl and vanadyl trichlorides might serve to throw additional light on this question of the relation of the specific volumes of the members of a family of elements to their atomic weights.

Methods of observation.—A detailed account of the methods of observation and of reduction and calculation employed in this series of researches is reserved for a subsequent communication; but in order to render certain of the data given in this paper more intelligible, it may be desirable to state that the rates of expansion of the various liquids have been determined in thermometer-shaped vessels (dilatometers), graduated and accurately calibrated. The readings were made with a telescope provided with a micrometer eyepiece. Three series of thermometers were employed, two of which were obtained from Mr. Casella, and the third from Dr. Geissler, of Bonn; for a description of these instruments I refer to the paper by Prof. Rücker and myself on the "Expansion of Sea-water by Heat"†.

All observations of temperature, unless otherwise stated, are converted into air-thermometer degrees by means of Regnault's and Recknagel's Tables‡. In the determination of the boiling-points the bulb of the thermometer was placed in the vapour of the liquid. I mention this fact as serving to account for the discrepancy in the numbers given by Pierre and myself, Pierre's observations being made with the bulb in the liquid.

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probable number 122·3 (Dexter, Kessler) be adopted, the specific volume is found to approximate more nearly to that of phosphorus and arsenic; at least the variation from the mean value for the two last-named elements is less than the difference between the specific volumes of tin and titanium, which are regarded by Kopp as practically identical.

* Proc. Roy. Soc. vol. xxiii. p. 364. Ber. Deut. Chem. Gesell. 1875, p. 326.

† *Antè*, p. 159.

‡ Wüllner's Lehrbuch der Physik. Pogg. Ann. cxxiii. p. 115.

Due precaution was taken to ensure regular ebullition and to prevent over-heating. In correcting the indications of the thermometer for the cooled portion of the column, I have made use of a special series of observations to obtain the value of δ in the well-known expression

$$T=t+\delta(t-t')n,$$

in which

t=the observed temperature on the thermometer,

t'=the mean temperature of the cooled column,

n=the length of column, measured in degrees, possessing the temperature t',

δ=a constant, usually taken as ·000154, *i. e.* the value of the apparent expansion of mercury in glass for 1°,

since it is evident, as pointed out by Holtzmann and by Wüllner and Landolt*, that by taking δ=·000154 the results are over-corrected when n is small. The barometric observations are corrected and reduced by the aid of Schumacher's Tables. The corrected boiling-points are reduced to the uniform pressure of 760 millims. by means of the formula

$$0{\cdot}0375^\circ(760-h),$$

in which h is the actual height of the barometer at the time of observation. As is well known, this expression does not afford absolutely accurate results, since the relation of the boiling-point to pressure differs with each liquid; nevertheless the results are more nearly comparable by adopting it than by neglecting it altogether. In one or two cases I have reduced the indications by the aid of data derived from vapour-tension observations when these have been to hand, the difference between the results thus afforded and those obtained by means of the formula above given has never exceeded 0°·05 C.; hence we may assume that for the ordinary range of barometric pressure the formula is generally applicable.

The specific gravities of the various liquids were taken at the temperature of melting ice, and are compared with water at 4°. The weighings were made by the method of vibrations, and are reduced to a vacuum. The results thus obtained, and also those calculated for the boiling-points, express the weights in grams of 1 cubic centimetre of the several liquids at these temperatures. The values given for the specific volumes indicate therefore the volume in cubic centimetres of equivalent weights in grams of the respective liquids at their boiling-points.

I. *Phosphoryl Trichloride.*

Prepared by heating phosphorus pentachloride with phosphorus pentoxide. The product commenced to boil at 107°, the greater portion distilling at 107°·5 (uncor.), under a barometric pressure of 755·2 millims. Since this boiling-point is about 2°·5 lower than that usually assigned to

* Ann. der. Chem. u. Pharm. Suppl. 1867–68, p. 140.

this compound, I solidified the chloride in a freezing-mixture of ice and salt, allowed it to melt partially, and poured away the liquid portion. This operation was repeated several times in order to remove any trichloride which might possibly be present. The boiling-point of the chloride was, however, unaltered by this treatment; the liquid distilled completely between 107° and 107°·5, the greater portion boiling at 107°·30, under a pressure of 751 millims. Corrected and reduced boiling-point 107°·23.

A second preparation made by Gerhardt's method, *i. e.* by heating phosphorus pentachloride with crystallized boric acid, boiled at 107°·4, under a pressure of 765 millims. Corrected boiling-point 107°·22.

The first sample was analyzed with the following results :—

I.	Weight of $POCl_3$ *in vacuo*	....	1·3156 gram.
	Weight of AgCl ,,	....	3·6907 grams.
II.	Weight of $POCl_3$,,	....	1·4364 gram.
	Weight of AgCl ,,	....	4·1064 grams.

	Calculated.	Found. I.	Found. II.
Chlorine	69·36 per cent.	69·37	69·39

Three determinations of specific gravity made with different bottles gave the following numbers :—

I.	1·71185
II.	1·71189
III.	1·71182
Mean	1·71185 at 0°

compared with water at same temperature; compared with water at 4° the specific gravity is 1·71163.

The rate of expansion of phosphoryl trichloride from 0° to its boiling-point may be accurately represented by the expression

$$V = 1 + 0{\cdot}001\,064\,309t + 0{\cdot}000\,001\,126\,66t^2 + 0{\cdot}000\,000\,005\,299t^3.$$

By means of this formula the following Table, showing the true volume of phosphoryl trichloride at every 10° between 0° and 110°, has been calculated :—

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		70	108184	1278
10	101076	1076	80	109507	1323
20	102178	1102	90	110878	1371
30	103309	1131	100	112300	1422
40	104471	1162	110	113776	1476
50	105669	1198			
60	106906	1237	107·23	1·133615	

The specific gravity of phosphoryl trichloride at 107°·23 is 1·50987; hence its specific volume $= \frac{153·38}{1·50987} = 101·58$.

The specific gravity of this compound at 10°, at 51°, and at its boiling-point has already been determined by H. L. Buff*. The results of his observations, compared with mine for the above temperatures, are given below; the specific gravities are compared with water at 0°.

	10°.	51°.	Boiling-point.
Buff........	1·6937	1·6494 (? 1·6194)	1·5090 (110°)
Thorpe	1·6936	1·6181	1·51008 (107°·23)

The specific volume of phosphoryl trichloride, calculated from Buff's numbers, is 101·6.

II. *Vanadyl Trichloride.*

This compound was prepared by heating vanadium trioxide, obtained by reducing the pentoxide by means of hydrogen gas, in a stream of dry chlorine. I am indebted to Dr. Roscoe for the pentoxide; it was a portion of the sample employed by him in determining the atomic weight of vanadium, and had been prepared with great care; it was beautifully crystalline and of a magnificent ruby-red colour†. In order to free the vanadyl trichloride from dissolved chlorine, it was maintained at a temperature near its boiling-point for a couple of hours in a current of dry carbon dioxide. The chloride was distilled into the flask in which its boiling-point was to be determined. Therm. Casella C. The liquid commenced to boil at 127°·2; the column rapidly rose to 127°·3, at which point it remained constant. $n=10°$, $t'=30°$. Bar. 764·5 millims. Correction for scale-error on thermometer −0°·15. Corrected boiling-point 127°·29. Corrected and reduced boiling-point 127°·19.

The results obtained with the dilatometer may be represented by the formula

$$V=1+0·000\,965\,236t+0·000\,000\,898\,26t^2 +0·000\,000\,003\,191\,63t^3,$$

by means of which is calculated the following Table, showing the true volumes of vanadyl trichloride for every 10° between 0° and 130°:—

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		80	108460	1154
10	100975	975	90	109647	1187
20	101969	994	100	110870	1223
30	102985	1016	110	112129	1259
40	104025	1040	120	113428	1299
50	105091	1066	130	114767	1339
60	106184	1093			
70	107306	1122	127·19	1·143867	

* Ann. Chem. Pharm. Suppl. vol. iv. p. 184.

† Phil. Trans. 1867, p. 1.

The mean of three experiments gives the specific gravity of vanadyl trichloride at 0°, compared with water at 4°, as 1·86527. Roscoe found 126°·7 for the boiling-point of this compound, and for its specific gravity

1·841 at 14°·5	reduced	1·8655 at 0°
1·836 at 17°·5	,,	1·8653 ,,
1·828 at 24°	,,	1·8665 ,,

The reduced sp. gr. (S_0) in this and the following cases has been calculated by means of the expression

$$S_0 = S_t \frac{V'}{V},$$

in which

S_t = the sp. gr. at the higher temperature t,

V' = the volume of the liquid at t, obtained by the interpolation formula.

V = volume of the water at t (vol. at 4° = 1), obtained from Rossetti's Tables*.

The indications of the dilatometer have been controlled by determining the degree of expansion suffered by the vanadyl trichloride on being heated in the specific-gravity bottle from 0° to near 100°, *i. e.* in the steam from boiling water. The details of the experiments are as follows:—

Experiment I. Weight of $VOCl_3$ at 10° *in vacuo* 7·15114 grams.
Weight of $VOCl_3$ *in vacuo* after having been heated to 100°·37. Bar. 770·3 millims. .... 6·46541 ,,
Expansion of glass for 1°...... ·00002633

Hence 10,000 vols. at 0° become at 100°·37—

Observed 11090
Calculated from formula 11091

Experiment II. Weight of $VOCl_3$ at 0° *in vacuo* 7·15156 grams.
Weight of $VOCl_3$ *in vacuo* after having been heated to 100°·10. Bar. 762·9 millims......... 6·46736 ,,
Expansion of glass for 1° .... ·00002633

Hence 10,000 vols. at 0° become at 100°·10—

Observed 11087
Calculated from formula 11088

The agreement between the results is satisfactory. The control is important, since it might be supposed, from Matthiessen's criticism of Kopp's observations on the expansion of water, that the dilatometric

* Ann. de Chim. et de Phys. x. 1867, xvii. 1869. Mean results of the observations of Kopp, Pierre, Despretz, Haagen, Matthiessen, Weidner, Kremers, and Rossetti.

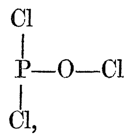
method of determining the expansion of liquids tends to give low results*.

The specific gravity of vanadyl trichloride at 127°·19 is 1·63067; hence its specific volume is $\frac{173{\cdot}73\dagger}{1{\cdot}63067} = 106{\cdot}54$.

It is thus evident that the specific volumes of vanadyl and phosphoryl trichlorides are not equal; the compound with the higher molecular weight has the greater specific volume.

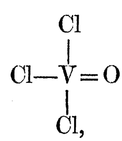
In the communication on the chlorides of phosphorus already referred to, it is shown that if we assume, as appears in the highest degree probable, that there is a relation between the manner in which the oxygen atoms in a compound are held in union and their specific volume, it follows that the oxygen atom in $POCl_3$ possesses the smaller of the two values 12·2 and 7·8 assigned by Kopp to oxygen, and accordingly that this atom is attached to the phosphorus by only one combining unit.

Thus



showing that the phosphorus atom in phosphoryl trichloride possesses the same atomic value as in phosphorus trichloride.

As the difference between the two values for the volume of oxygen, viz. 12·2 − 7·8 = 4·4, is but little less than that between the specific volumes of $VOCl_3$ and $POCl_3$, viz. 106·54 − 101·58 = 4·96, it is possible that the difference in the specific volumes of the two liquids may be due to the different manner in which the oxygen atoms are united to the vanadium and phosphorus atoms; for, if V be regarded as a pentad, $VOCl_3$ must be written



the oxygen atom having the value 12·2. Assuming Kopp's value for Cl, viz. 22·8, this would leave for P and V nearly the same specific volume, viz.

P	25·4
V	25·9

From the uncertainty respecting the particular volume to be assigned to the oxygen atom in vanadyl trichloride, our knowledge of the specific volumes of $VOCl_3$ and $POCl_3$ gives us little aid towards solving the question whether the several members of a family of elements have identical specific volumes.

* Phil. Trans. 1866.

† V = 51·35, Roscoe; Cl = 35·46, Stas.

With a view to obtain further evidence, I have redetermined with special care the boiling-points, specific gravities, and rates of expansion of the tetrachlorides of silicon, titanium, and tin.

The atomic weights of Si and Ti and of P and V show about the same gradational difference :—

Si........	28·10	P........	31·00
Ti........	50·00	V........	51·35

And since the tetrachlorides are free from oxygen, the uncertainty arising from the variable specific volume of that element is eliminated. I have also compared the specific volumes of the trichlorides of phosphorus, arsenic, and antimony, making use of Kopp's determination in the case of the last-named compound. We thus obtain material for the discussion of the question from analogous derivatives of two well-defined groups of elements, viz. :—

Si........	28·10	P........	31·00
Ti........	50·00	V........	51·35
		As	75·15
Sn	118·10	Sn	122·30

III. *Silicon Tetrachloride.*

This compound was prepared in the ordinary way by heating a mixture of pure silica and lampblack (previously ignited in chlorine) in a current of dry chlorine gas. The product was distilled repeatedly over sodium. It boiled constantly between 58° and 58°·3, the greater portion coming over at 58°·2.

Corrected boiling-point 57°·95. Bar. 765·35 millims. Corrected and reduced boiling-point 57°·57.

Its specific gravity at 0°, compared with water at 4°, is 1·52408. Other observations on record are :—

	Boiling-point. °	Barom. millim.	Sp. gr.	Compared with water at 4°. °
Pierre*	59·0	760·1	1·52371 at 0°	1·52371 at 0
Regnault†..	56·81	760·0	——	——
Haagen‡ ..	58·0	756·0	1·4878 at 20°	1·52644 ,,
?Mendelejeff	——	——	1·50068 at 10°·98	1·52266 ,,
Mendelejeff§	——	——	1·4928 at 15°	1·52230 ,,

Two series of observations of the expansion of silicon tetrachloride were made. The results of the first series may be accurately represented by the formula

$$V = 1 + 0{\cdot}001\,337\,14t + 0{\cdot}000\,002\,618\,01t^2 + 0{\cdot}000\,000\,003\,907\,62t^3. \quad . \quad . \quad . \text{ (I.)}$$

* Ann. de Chim. et de Phys. xx. [3], p. 26.

† From vapour-tension observations.

‡ Pogg. Ann. cxxxi. p. 117.

§ Jahresbericht, xiii. p. 7.

The second series of observations may with equal accuracy be represented by the expression

$$V=1+0{\cdot}001\,324\,75\,t + 0{\cdot}000\,003\,001\,54\,t^2 + 0{\cdot}000\,000\,000\,405\,511\,t^3 \quad . \quad . \quad . \quad (II.)$$

The mean formula is

$$V=1+0{\cdot}001\,330\,946\,t + 0{\cdot}000\,002\,809\,78\,t^2 + 0{\cdot}000\,000\,002\,156\,57\,t^3, \quad . \quad . \quad (III.)$$

by the aid of which the following Table, showing the true volumes of silicon tetrachloride for every 5° between 0° and 60°, has been calculated:—

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		40	105787	775
5	100673	673	45	106578	791
10	101359	686	50	107384	806
15	102060	701	55	108206	822
20	102776	716	60	109044	838
25	103506	730			
30	104252	746	57·57	1·086346	
35	105012	760			

The specific gravity at the boiling-point is 1·40295, and the specific volume $= \frac{169{\cdot}94^*}{1{\cdot}40295} = 121{\cdot}13$.

Pierre has given the following expression for the expansion of this liquid†:—

$$V=1+0{\cdot}001\,294\,119\,069\,t + {\cdot}000\,002\,184\,143\,631\,t^2 + {\cdot}000\,000\,040\,864\,220\,t^3.$$

This formula represents a curve slightly differing in character from that afforded by my observations, as is evident from the following comparison. The temperature in this and the following comparisons is given in degrees of the mercurial thermometer.

	10°	20°	30°	40°	50°
Pierre	1·01320	1·02708	1·04189	1·05804	1·07527
Thorpe	1·01349	1·02757	1·04226	1·05756	1·07352

The specific volume of silicon tetrachloride, calculated from Pierre's results, is $\frac{169{\cdot}94}{1{\cdot}39502} = 121{\cdot}82$.

IV. *Titanium Tetrachloride.*

I am indebted to Mr. Phillips Bedson, B.Sc., of Owens College, for a liberal supply of a pure specimen of this liquid. On distillation it commenced to boil at 135°·8; the column rapidly rose to 135°·9, at which

* Si=28·10, Dumas; Cl=35·46, Stas. † *Loc. cit.*

point the liquid boiled constantly. $t=135^{\circ}\cdot9$, $n=19^{\circ}\cdot9$, $t'=24^{\circ}\cdot5$. Bar. 752·6 millims. Corrected boiling-point 136°·03. Corrected and reduced boiling-point 136°·41.

Its specific gravity at 0°, compared with water at 4°, was found to be 1·76041. According to Pierre titanium chloride boils at 136° under a pressure of 762·3 millims., and has a specific gravity of 1·76088 at 0° compared with water at 4° *.

Observations with the dilatometer have led to the formula

$$V=1+0\cdot000\,982\,612t+0\cdot000\,000\,505\,528t^2 + 0\cdot000\,000\,005\,130\,52t^3,$$

by means of which the following Table has been calculated:—

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		90	109627	1180
10	100988	988	100	110845	1218
20	101990	1002	110	112103	1258
30	103007	1017	120	113406	1303
40	104044	1037	130	114756	1350
50	105104	1060	140	116155	1399
60	106189	1085			
70	107302	1113	136·41	1·156467	
80	108447	1145			

The specific gravity of the liquid at 136°·41 is 1·52223, and the specific volume $=\frac{191\cdot84\dagger}{1\cdot52223}=126\cdot025$.

According to Pierre the expansion of titanium tetrachloride may be represented by the formula ‡

$$V=1+0\cdot000\,942\,569\,004t+0\cdot000\,001\,345\,791\,937t^2 + 0\cdot000\,000\,000\,888\,044t^3,$$

which gives results agreeing well with those afforded by my observations, as the following comparison shows:—

	30°	60°	90°	120°
Pierre........	1·02951	1·06159	1·09638	1·13402
Thorpe	1·02989	1·06169	1·09621	1·13414

The specific volume of titanium chloride, calculated from Pierre's results, is $\frac{191\cdot84}{1\cdot52415}=125\cdot867$.

V. *Tin Tetrachloride.*

Prepared by heating pure tin in a current of dry chlorine and expelling the dissolved gas by repeated distillation in a stream of dry carbon

* *Loc. cit.* p. 21.

† Ti=50·00, Pierre; Cl=35·46, Stas.

‡ *Loc. cit.* p. 20.

dioxide. The liquid commenced to boil at 113°·4; the column quickly rose to 113°·5, and then slowly to 113°·55, between which points nearly the entire amount passed over. $t=113°·55$, $n=6°·55$, $t'=24°·5$. Bar. 750·8 millims. Corrected boiling-point 113°·50. Corrected and reduced boiling-point 113°·89.

Its specific gravity at 0°, compared with water at 4°, was found to be 2·27875. Other observers have found:—

	Boiling-point. °	Bar. millim.		Sp. gr. compared with water at 4° C.
Pierre*	115·4	753·1	....	2·26712
Dumas†	120	767		——
Andrews‡	112·5	752		——
Haagen§......	112·0	754·9	2·2328 at 20°	=2·28137

Two independent series of observations on the rate of expansion of the tin tetrachloride were made. The first series has afforded the formula

$$V=1+0·001\,161\,138t+0·000\,000\,641\,935t^2+0·000\,000\,007\,730\,07t^3 \quad \text{(I.)}$$

The formula given by the second series is

$$V=1+0·001\,159\,962t+0·000\,000\,650\,399t^2+0·000\,000\,007\,724\,12t^3 \quad \text{(II.)}$$

The mean formula is

$$V=1+0·001\,160\,55t+0·000\,000\,646\,167t^2+0·000\,000\,007\,727\,1t^3, \quad \text{(III.)}$$

by means of which the following Table, showing the volume of tin tetrachloride at every 10° between 0° and 115°, has been calculated:—

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		80	110094	1388
10	101168	1168	90	111532	1438
20	102353	1185	100	113024	1492
30	103561	1208	110	114576	1552
40	104795	1234	115	115376	800
50	106061	1266			
60	107363	1302	113·89	1·151971	
70	108706	1343			

The specific gravity at 113°·89 is 1·97813; hence the specific volume is

$$\frac{259·94\,\|}{1·97813}=131·407.$$

* *Loc. cit.* p. 19.
† Clarke's Nat. Constants.
‡ Clarke's Nat. Constants.
§ Pogg. Ann. vol. cxxxi. p. 117.
‖ Sn=118·10, Dumas; Cl=35·46, Stas.

Pierre represents the expansion of this liquid by the equation * :—

$$V = 1 + 0{\cdot}001\,132\,800\,769t + 0{\cdot}000\,000\,911\,710\,706t^2 + 0{\cdot}000\,000\,007\,579\,789t^3,$$

which gives results somewhat lower than those afforded by formula III.

	20°.	40°.	60°.	80°.	100°.
Pierre....	1·02308	1·04726	1·07289	1·10034	1·12998
Thorpe ..	1·02347	1·04771	1·07340	1·10080	1·13024

The specific volume of tin tetrachloride, calculated from Pierre's observations, is $\frac{259{\cdot}94}{1{\cdot}96373} = 132{\cdot}371$.

The results of the determinations of the specific volumes of the tetrachlorides of silicon, titanium, and tin, liquids of analogous constitution and all derivatives of the tetrad group of elements, serve to establish the conclusion, indicated by the difference in the specific volumes of phosphoryl and vanadyl trichlorides, that the specific volumes of the several members of a family of elements are not identical, but that the values increase with the increase of the atomic weight of the members.

	Molecular weight.	Specific volume.
$SiCl_4$	169·94	121·13
$TiCl_4$	191·84	126·03
$SnCl_4$	259·94	131·41

It is also noteworthy that the difference between the specific volumes of tin and titanium tetrachlorides is almost the same as the difference between the specific volumes of vanadyl and phosphoryl trichlorides; it has already been remarked that the difference between the atomic weights of vanadium and phosphorus is nearly the same as that between the atomic weights of titanium and silicon.

	Mol. weight.	Diff.	Spec. vol.	Diff.
$POCl_3$	153·38	20·35	101·58	4·96
$VOCl_3$	173·73		106·54	
$SiCl_4$	169·94	21·90	121·13	4·90
$TiCl_4$	191·84		126·03	

It would seem from this that the constitution of vanadyl trichloride is similar to that of the phosphoryl compound, and must therefore be expressed by the formula

Cl
|
V—O—Cl
|
Cl,

in which V appears as a triad, the oxygen atom having the same specific

* *Loc. cit.* p. 20.

volume as in phosphoryl trichloride. On the other hand, the order of the divergences shown by P, As, and Sb (*vide infrà*), would appear to indicate that V may be pentad in this compound, whence O would have the volume 12·2.

Comparison of the specific volumes of PCl_3, $AsCl_3$, and $SbCl_3$:—

VI. *Phosphorus Trichloride.*

I prepared this compound by heating purified amorphous phosphorus in dry chlorine gas. The reaction is very regular, and large quantities of the liquid may be thus obtained with great ease and rapidity. The product was digested with ordinary phosphorus for some weeks to remove the last trace of free chlorine. On distillation the liquid commenced to boil at 76°·05, and all came over below 76°·25, the most constant point appearing to be at 76°·15. $n=18°·2$, $t'=26°·0$. Bar. 768·2 millims. Corrected and reduced boiling-point 75°·95. Two determinations of specific gravity gave—

I.	1·61290
II.	1·61299
Mean	1·61294 at 0°

compared with water at 0°; compared with water at 4° its specific gravity is 1·61275.

Other observers have found for the boiling-point and specific gravity of phosphorus trichloride :—

	B.P. °	Bar. millim.		Sp. gr. at 0° compared with water at 4°.
Pierre*	78·34	751·5	....	1·61616
H. L. Buff† ..	76·0	760·0	1·61191 at 0°‡	1·61170
Haagen§	76·0	745·9	1·5774 at 20°	1·61165

The observations with the dilatometer have led to the formula

$$V=1+0·001\,139\,37t+0·000\,001\,668\,07t^2 \\ +0·000\,000\,004\,012t^3,$$

by means of which the following Table, showing the true volume of phosphorus trichloride at every 10° between 0° and 80°, has been calculated :—

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		50	106164	1314
10	101156	1156	60	107523	1359
20	102349	1193	70	108931	1408
30	103579	1230	80	110388	1457
40	104850	1271			
			75·90	1·09784	

* *Loc. cit.* p. 9. † Ann. der Chem. und Pharm. Suppl. vol. iv. p. 184.
‡ Mean of 1·61253 and 1·61128, compared with water at 0°. § *Loc. cit.*

The specific gravity at 75°·90 is 1·46900, and accordingly the specific volume is $\frac{137·38}{1·4690}=93·52$.

Pierre has found that the expansion of phosphorus chloride may be represented by the formula*

$$V=1+0·001\,128\,618\,932t+0·000\,000\,872\,880\,045t^2 + 0·000\,000\,017\,923\,565t^3,$$

which gives results agreeing fairly well with those calculated by means of the expression deduced from my observations.

	10°.	30°.	50°.	70°.
Pierre	1·01139	1·03513	1·06085	1·08943
Thorpe	1·01147	1·03557	1·06138	1·08911

The specific gravity of phosphorus trichloride at various temperatures has also been determined by Buff†. The results of the several observations are:—

	Sp. gr. at B.P.	B.P.	Spec. vol.
Buff........	1·47102	76·0	93·39
Pierre	1·46601	78·34	93·71
Thorpe	1·46900	75·90	93·52
		Mean	93·54

VII. *Arsenic Trichloride.*

This compound was obtained by heating arsenic trioxide in a current of dry chlorine. It was distilled upwards in a current of dry carbon dioxide for some time in order to expel the excess of chlorine. Care is necessary to obtain a perfectly clear product; the least trace of moisture renders the liquid turbid from the formation of the insoluble oxychloride, AsClO. On distillation the liquid commenced to boil at 129°·23, and all came over below 129°·33, the greater portion boiling at 129°·30. $n=16°$, $t'=15°·5$. Bar. 733·4 millims. Corrected and reduced boiling-point 130°·21.

Its specific gravity at 8°·08, compared with water at the same temperature, was 2·18761; compared with water at 4° its specific gravity is found to be 2·20500.

Other observers have given for the boiling-point and specific gravity of arsenic trichloride—

	B.P. °	Bar. millim.		Sp. gr. compared with water at 4°.
Pierre	133·81	765·9	....	2·20495 at 0°
Haagen	128·0	754·0	2·1668 at 20°	2·20671 ,,

* *Loc. cit.* p. 10. The third term is erroneously printed 0·0000179 ....

† *Loc. cit.*

The observations with the dilatometer have afforded the formula

$$V = 1 + 0{\cdot}000\,991\,338\,5t + 0{\cdot}000\,000\,849\,14t^2 + 0{\cdot}000\,000\,002\,755\,08t^3,$$

by the aid of which the following Table is obtained; it shows the volume of arsenic trichloride at every 10° between 0° and 130°, the volume at 0° being taken as 100,000.

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		80	108615	1165
10	101000	1000	90	109811	1196
20	102019	1019	100	111038	1227
30	103058	1039	110	112299	1261
40	104119	1061	120	113595	1296
50	105203	1084	130	114928	1333
60	106313	1110			
70	107450	1137	130·21	1·14956	

The specific gravity of arsenic trichloride at 130°·21 is 1·91812; hence its specific volume is $\frac{181{\cdot}53^*}{1{\cdot}91812} = 94{\cdot}64$.

Pierre represents the expansion of this liquid by the expression†

$$V = 1 + 0{\cdot}000\,979\,072\,746t + 0{\cdot}000\,000\,966\,948\,2t^2 + 0{\cdot}000\,000\,001\,777\,204t^3,$$

which gives results uniformly lower than those afforded by my observations:—

	30°.	60°.	90°.	120°.
Pierre......	1·03029	1·06261	1·09724	1·13448
Thorpe	1·03040	1·06295	1·09805	1·13602

The specific volume of arsenic trichloride deduced from Pierre's numbers is $\frac{181{\cdot}53}{1{\cdot}91304} = 94{\cdot}891$.

VIII. *Antimony Trichloride.*

The rate of expansion of this compound has been determined by Kopp, who has given the following formula to express his observations‡:—

$$V = 1 + 0{\cdot}000\,805\,4\delta + 0{\cdot}000\,010\,33\delta^2,$$

in which δ = the number of degrees above the melting-point of the body, 73°·2 (Kopp). According to Kopp antimony trichloride boils at 223°, under a pressure of 747·7 millims. Reduced boiling-point 223°·5. Its specific gravity at 73°·2, compared with water at 4°, is 2·6753; at 223°·5 it is 2·3377. Accordingly its specific volume $= \frac{228{\cdot}68\,\S}{2{\cdot}3377} = 97{\cdot}82$.

* As = 75·15, Kessler; Cl = 35·46, Stas. † *Loc. cit.*

‡ Ann. der Chem. und Pharm. vol. xcv. p. 350.

§ Sb = 122·3, Kessler, Dexter; Cl = 35·46, Stas.

The numbers representing the specific volumes of the trichlorides of phosphorus, arsenic, and antimony exhibit a gradational order similar to that shown by the volumes of the tetrachlorides of silicon, titanium, and tin, and also by the specific volumes of phosphoryl and vanadyl trichlorides:—

	Mol. weight.	Spec. vol.
PCl_3............	137·38	93·54
$AsCl_3$	181·53	94·64
$SbCl_3$	228·68	97·82

although the differences are much less than in the cases of the two latter groups. I intend to return to the question in subsequent communications.

II. "Researches upon the Specific Volumes of Liquids." By T. E. Thorpe, Ph.D., F.R.S.E., Professor of Chemistry in the Yorkshire College of Science, Leeds. Communicated by Prof. A. W. Williamson, For. Sec. R.S. Received February 9, 1876.

III. *On the Specific Volumes of Bromine and Iodine Monochloride, and of Ethene Bromide and Ethene Chloriodide.*

The molecular weight of bromine is, as is well known, nearly equal to the arithmetic mean of the molecular weights of chlorine and iodine: hence the molecular weights of bromine and of iodine monochloride (I Cl) are nearly identical. These substances closely resemble each other in physical properties. Both are dark-red liquids about three times heavier than water. Bromine boils at about 59°·5, and solidifies at −24°·5; iodine monochloride melts at +24°·5, and boils at 101°: the interval between the boiling- and melting-points of the two compounds is approximately equal.

It appeared to me of interest to determine (1) if the specific volumes of these liquids exhibit a relation similar to that which is shown by their molecular weights, and (2) if the relation in their specific volumes is preserved in analogous combinations of the two bodies. I have accordingly determined the specific gravities, boiling-points, and rates of expansion of bromine and iodine monochloride, and of the compounds which these substances form by their union with ethene, C_2H_4. The observations will also serve to determine if bromine and iodine monochloride preserve, when in combination, the volumes which they possess in the free state.

I. *Bromine.*

About a kilogramme of the purest commercial bromine, dehydrated by agitation with pure and strong sulphuric acid, was carefully distilled, and the fraction boiling at about 60°, which amounted to about two