XXI.—*On the Relation between the Molecular Weights of Substances and their Specific Gravities when in the Liquid State.*

By T. E. THORPE, Ph.D., F.R.S.

(Continued from p. 225.)

Silicon Tetrachloride, SiCl_4 .

PREPARED by heating a mixture of pure precipitated silica and lamp-black (previously ignited in chlorine) in a current of dry chlorine gas. The product was repeatedly distilled over sodium. It boiled constantly between 58° and $58\cdot3^\circ$, the greater portion coming over at $58\cdot2^\circ$. $n = 0$, $t = 0$. Bar. $765\cdot35$ mm. Corrected and reduced boiling point $57\cdot57^\circ$.

Its specific gravity at 0° compared with water at 4° is $1\cdot52408$.

Other observations on record are—

	Boiling point.	Bar.	Specific gravity.	Compared with water at 4°.
Pierre	59·0° at 760·1 mm. (from vapour tension determinations)		1·52371 at 0°	1·52371 at 0°
Regnault	56·81° at 760·0 mm.		—	—
Haagen	58·0 „ 756·0 „		1·4878 at 20°	1·52644 „
Mendelejeff [?] ...	—	—	1·50068 at 10·98°	1·52266 „
Mendelejeff	—	—	1·4928 „ 15°	1·52230 „

The following observations were made in Dilatometer B:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2852·7	2852·7	31·61	2978·4	2978·4
6·25	2876·2	2876·1	36·81	3000·8	3000·7
10·50	2892·6	2892·6	42·09	3023·7	3023·8
15·81	2913·6	2913·4	47·57	3048·4	3048·3
20·95	2934·4	2934·1	52·36	3070·0	3070·1
26·25	2955·7	2955·9	57·44	3093·8	3093·7

These observations may be represented by the formula—

$$2852\cdot720 + 3\cdot706\,398t + 0\cdot008\,468\,05t^2 + 0\cdot000\,000\,940\,875t^3,$$

which affords the numbers seen in the third column of the preceding table.

A second series of observations was made in Dilatometer C, with the following results:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2960·4	2960·2	31·63	3091·0	3091·1
6·25	2984·8	2984·8	36·81	3114·4	3114·2
10·50	3001·8	3001·9	42·10	3138·2	3138·2
15·81	3023·7	3023·6	47·57	3163·8	3163·6
20·95	3045·2	3045·1	52·37	3186·1	3186·3
26·25	3067·6	3067·7	57·44	3210·8	3210·8

These numbers afford the following formula:—

$$2960\cdot239 + 3\cdot885\,145t + 0\cdot007\,653\,974t^2 + 0\cdot000\,011\,378\,46t^3,$$

which gives the volumes contained in the third column of the table.

Dividing through by the first terms, and correcting for the expansion of the glass, these formulæ become respectively—

$$I. \quad V = 1 + 0\cdot001\,324\,75t + 0\cdot000\,003\,001\,54t^2 + 0\cdot000\,000\,000\,405\,511t^3,$$

and

$$\text{II. } V = 1 + 0.001\,337\,143t + 0.000\,002\,618\,01t^2 + 0.000\,000\,003\,907\,62t^3,$$

The mean formula is—

$$V = 1 + 0.001\,330\,946t + 0.000\,002\,809\,78t^2 + 0.000\,000\,002\,156\,57t^3,$$

which affords the numbers given in the following table, expressing the relative volumes of silicon tetrachloride at every 5° between 0° and 60°.

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	35	105012	760
5	100673	673	40	105787	775
10	101359	686	45	106578	791
15	102060	701	50	107384	806
20	102776	716	55	108206	822
25	103506	730	60	109044	838
30	104252	746	57.57	1.086346	—

According to Pierre the expansion of silicon tetrachloride may be expressed by the formula—

$$V = 1 + 0.001\,294\,119\,069t + 0.000\,002\,184\,143\,631t^2 + 0.000\,000\,040\,864\,220t^3.$$

which represents a curve differing slightly from that afforded by my observations, as will be seen from the following comparison :—

	10°.	20°.	30°.	40°.	50°.
Pierre ..	101320	102708	104189	105804	107527
Thorpe..	101349	102757	104226	105756	107352

Titanium Tetrachloride, TiCl₄.

I am indebted to Dr. Bedson, of Owens College, for a liberal supply of the pure liquid. On distillation it began to boil at 135.8°; the column rapidly rose to 135.9°, at which point the liquid boiled constantly. $n = 19.9$, $t = 24.5^\circ$. Bar. 752.6 mm. Corrected and reduced boiling point 136.41°.

Its specific gravity at 0° compared with water at 4° was 1.76041. According to Pierre this liquid boils at 136° under a pressure of 762.3 mm., and has a specific gravity of 1.76088 at 0° compared with water at 4°.

The following observations of the rate of expansion were made with Dilatometer C.

In the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2971·0	2970·6	36·93	3078·4	3078·4
12·28	3005·7	3005·8	49·19	3115·6	3115·8
24·72	3041·8	3042·0	61·40	3154·4	3154·2

In the oil-bath :—

T°.	t°.	T Δ .	V.	E.	Observed.	Calculated.
38·55	19·6	38·45	3082·1	53·3	3083·0	3083·0
46·87	21·2	46·85	3106·7	78·0	3108·7	3108·6
64·11	25·1	63·99	3157·4	128·7	3162·5	3162·5
74·09	26·3	74·06	3187·6	158·9	3195·4	3195·4
86·49	27·7	86·64	3225·6	196·9	3237·7	3237·8
98·76	29·6	99·17	3264·3	235·6	3281·7	3281·7
113·43	30·4	113·55	3308·6	279·9	3333·8	3334·4
123·46	32·5	123·66	3341·8	313·1	3373·4	3373·1
135·41	34·7	135·87	3381·8	353·0	3422·1	3421·8

These observations afford the formula—

$$2970\cdot586 + 2\cdot845\ 56t + 0\cdot001\ 431\ 43t^2 + 0\cdot000\ 015\ 205\ 3t^3,$$

which on dividing through by the first term and correcting for the expansion of the glass becomes—

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

and this affords the numbers given in the following table. It shows the relative volumes of titanium tetrachloride at every 5 Δ between 0 Δ and 140 Δ .

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	75	107870	568
5	100493	493	80	108447	577
10	100988	495	85	109033	586
15	101487	499	90	109627	594
20	101990	503	95	110231	604
25	102496	506	100	110845	614
30	103007	511	105	111469	624
35	103523	516	110	112103	634
40	104044	521	115	112749	646
45	104571	527	120	113406	657
50	105104	533	125	114075	669
55	105643	539	130	114756	681
60	106188	545	135	115448	692
65	106741	553	140	116155	707
70	107302	561	136·41	1·156467	—

Pierre, who has also observed the thermal expansion of this liquid, finds that its rate may be represented by the formula—

$$V = 1 + 0.000\,942\,569\,004t + 0.000\,001\,345\,793\,937t^2 + 0.000\,000\,000\,888\,044t^3,$$

which gives results agreeing with those afforded by my observations.

	30°.	60°.	90°.	120°.
Pierre	102951	106159	109638	113402
Thorpe	102989	106169	109621	113414

Tin Tetrachloride, SnCl₄.

I prepared this liquid by heating pure tin in a current of dry chlorine, and expelling the dissolved gas by repeated distillation in a stream of dry carbon dioxide. The liquid boiled very constantly at 113.55°; t 24.5; $n = 6.5$. Bar. 750.8 mm. 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.	Sp. gr. at 0° compared with water at 4°.
Pierre	115.4 at 753.1 mm.	2.26712
Dumas	120 „ 767 „	—
Andrews	112.5 „ 752 „	—
Haagen	112.0 „ 754.9 „	2.2328 at 20° 2.28137

The following observations of the thermal expansion were made in Dilatometer C.

In the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	2961.2	2960.9	40.99	3103.5	3103.3
10.16	2995.0	2995.2	51.14	3140.5	3140.6
20.42	3030.3	3030.5	61.38	3179.5	3179.4
30.84	3066.9	3066.9			

In the oil-bath :—

T°.	t° .	TA.	V.	E.	Observed.	Calculated.
72.17	23.1	72.12	3211.1	182.4	3222.1	3221.4
82.44	25.3	82.73	3248.3	219.5	3263.8	3264.5
92.46	28.3	92.69	3286.0	257.3	3307.0	3306.3
102.59	31.2	103.06	3324.3	295.5	3351.5	3351.8
112.67	31.4	112.79	3360.6	331.9	3396.0	3396.2

These observations may be represented by the formula—

$$2960\cdot868 + 3\cdot361\,36t + 0\cdot001\,842\,72t^2 + 0\cdot000\,022\,824\,6t^3,$$

which gives the numbers in the third column of the above table.

A second series made in Dilatometer B gave the following results.

In the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2859·6	2859·1	41·00	2996·8	2996·7
10·16	2891·9	2892·3	51·14	3032·5	3032·6
20·42	2926·0	2926·3	61·38	3070·1	3070·1
30·84	2961·5	2961·5			

In the oil-bath :—

T° .	t° .	$T\Delta$.	V.	E.	Observed.	Calculated.
72·18	23·1	72·13	3099·9	188·3	3111·2	3110·7
82·45	25·3	82·74	3135·6	224·0	3151·6	3152·2
92·47	28·3	92·70	3171·6	260·1	3192·9	3192·7
102·57	31·2	103·04	3208·6	297·0	3236·1	3236·4
112·65	31·4	112·77	3243·7	332·1	3279·2	3279·1

These numbers lead to the formula—

$$2859\cdot053 + 3\cdot246\,85t + 0\cdot001\,752\,53t^2 + 0\cdot000\,022\,056t^3.$$

Dividing through by the first terms and correcting for the expansion of the glass, these formulæ become—

$$(I.) V = 1 + 0\cdot001\,159\,962t + 0\cdot000\,000\,650\,399t^2 + 0\cdot000\,000\,000\,724\,12t^3.$$

$$(II.) V = 1 + 0\cdot001\,161\,138t + 0\cdot000\,000\,641\,935t^2 + 0\cdot000\,000\,007\,730\,07t^3$$

The mean formula is—

$$V = 1 + 0\cdot001\,160\,55t + 0\cdot000\,000\,646\,167t^2 + 0\cdot000\,000\,007\,727\,1t^3,$$

by the aid of which the following table, showing the relative volume of tin tetrachloride at every 5^Δ between 0^Δ and 115^Δ , is calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	65	108029	666
5	100582	582	70	108706	677
10	101168	586	75	109394	688
15	101758	590	80	110094	700
20	102353	595	85	110806	712
25	102954	601	90	111532	726
30	103561	607	95	112271	739
35	104174	613	100	113024	753
40	104795	621	105	113793	769
45	105424	629	110	114576	783
50	106061	637	115	115376	800
55	106707	646	113·89	1·151971	—
60	107363	656			

Pierre represents the expansion of this liquid by the equation—

$$V = 1 + 0\cdot001\,132\,800\,769t + 0\cdot000\,000\,911\,710\,706t^2 + 0\cdot000\,000\,007\,579\,789t^3,$$

which gives somewhat lower results than those afforded by the mean formula deduced from my observations.

	20°.	40°.	60°.	80°.	100°.
Pierre. . .	102308	104726	107289	110334	112998
Thorpe ..	102347	104771	107341	110080	113024

Phosphorus Trichloride, PCl_3 .

This liquid was prepared by heating amorphous phosphorus in a stream of dry chlorine. The red phosphorus of commerce rarely contains more than from 90 to 95 per cent. of that modification of the element, and the ordinary phosphorus with which it is usually mixed gradually oxidises on exposure to air, forming oxy-acids which give the substance an acid reaction and render it hygroscopic. In order to obviate the possible formation of any oxy-chlorides of phosphorus from the presence of these substances, the red phosphorus was placed in a funnel, the neck of which was plugged with asbestos and repeatedly washed with water, afterwards with alcohol, and then with ether, and dried at a gentle heat. The action of chlorine on the heated red phosphorus is very regular, and large quantities of the trichloride may be thus obtained with great ease and rapidity. The product was digested for some weeks with a small quantity of ordinary phosphorus to remove free chlorine and afterwards distilled. It began to boil at $76\cdot05^\circ$, and all came over below $76\cdot25^\circ$, the larger portion distilling at about $76\cdot15^\circ$; $n = 18\cdot2$ $t = 26\cdot0$, bar. $768\cdot2$ mm.; corrected and reduced b. p. $75\cdot95^\circ$.

Two determinations of specific gravity at 0° gave—

I	1·61290
II	1·61299
Mean	1·61294

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

Other observations on record are—

	Boiling point.	Bar.	Sp. gr. at 0° compared with water at 4°.
Pierre	78·34°	at 751·5 mm.	1·61616
H. L. Buff ..	76·0	„ 760 „	1·61191 at 0°
Haagen	76·0	„ 745·9 „	1·5774 „ 20 1·61165

The following observations of the thermal expansion were made with Dilatometer B:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	2855·1	2854·8	44·36	3006·7	3006·6
6·30	2875·2	2875·3	50·76	3030·2	3030·3
12·66	2896·3	2896·3	57·30	3055·0	3055·1
19·01	2917·7	2917·7	63·84	3080·6	3080·5
25·32	2939·0	2939·1	70·28	3106·3	3106·2
31·87	2961·1	2961·9	76·03	3129·5	3129·8

These results may be expressed by the formula—

$$2854·84 + 3·236\ 18t + 0·003\ 047\ 8t^2 + 0·000\ 025\ 69t^3,$$

by means of which the numbers in the third column are calculated.

A second series made with Dilatometer C gave—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	2972·9	2972·7	44·36	3131·4	3131·1
6·29	2993·8	2994·0	50·75	3155·6	3155·7
12·66	3015·9	3015·9	57·30	3181·2	3181·6
19·01	3038·3	3038·2	63·83	3207·9	3207·9
25·32	3060·5	3060·7	70·31	3234·6	3234·7
31·84	3084·3	3084·3	76·01	3258·6	3258·8

These numbers may be represented by the expression—

$$2972·66 + 3·372\ 58t + 0·003\ 575\ 5t^2 + 0·000\ 020\ 81t^3.$$

On dividing through by the first terms respectively and correcting for the expansion of the glass, these formulæ become—

$$\text{I. } V = 1 + 0·001\ 159\ 1t + 0·000\ 001\ 096\ 5t^2 + 0·000\ 000\ 009\ 027t^3,$$

and

$$\text{II. } V = 1 + 0·001\ 159\ 2t + 0·000\ 001\ 230t^2 + 0·000\ 000\ 007\ 030t^3.$$

The mean formula is—

$$V = 1 + 0.001\,159\,2t + 0.000\,001\,163\,7t^2 + 0.000\,000\,008\,029t^3,$$

by means of which the following table, showing the relative volume of phosphorus chloride at every 5^Δ between 0^Δ and 80^Δ , is calculated—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	45	105525	651
5	100583	583	50	106187	662
10	101172	589	55	106861	674
15	101768	596	60	107547	686
20	102371	603	65	108247	700
25	102983	612	70	108960	713
30	103604	621	75	109687	727
35	104234	630	80	110429	742
40	104874	640	75.95	1.10827	—

Pierre found that the expansion of phosphorus trichloride might be represented by the formula—*

$$V = 1 + 0.001\,128\,619t + 0.000\,000\,872\,88t^2 + 0.000\,000\,017\,924t^3,$$

which gives results fairly accordant with those calculated from the mean formula obtained from my observations—

	10° .	30° .	50° .	70° .
Pierre	101139	103513	106085	108943
Thorpe.....	101161	103580	106159	108938

Phosphorus Tribromide, PBr₃.

A quantity of this liquid, prepared by direct synthesis and boiling between 168.5° and 171° , was carefully distilled, and the portion which came over between 169.3° and 170.5° , amounting to about four-fifths of the whole, was collected separately. On redistillation nearly the whole of this fraction boiled between 169.7° and 170.1° ; $n = 95$; $t = 19$; bar. 757.0 mm.; corrected and reduced b. p. 172.9^Δ .

The specific gravity of phosphorus tribromide at 0° , compared with water at the same temperature, was observed to be 2.92349; compared with water at 4^Δ it is 2.92311.

Pierre found the boiling point of this liquid to be 175.3° at 760.2 mm. and the specific gravity 2.92489 at 0° compared with water at 4^Δ .

The following observations were made in Dilatometer C.

* *Ann. Chim. Phys.*, 20 [3], 10. The third term is erroneously printed 0.000 179....

In the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2955·2	2955·8	43·21	3063·4	3063·4
14·24	2990·2	2990·5	57·56	3100·7	3100·9
28·73	3026·6	3026·5	72·18	3140·3	3140·1

In the oil-bath :—

T° .	t° .	$T\Delta$.	V.	E.	Observed.	Calculated.
72·01	21·1	71·97	3134·2	131·1	3140·0	3140·0
86·76	27·7	86·92	3172·1	169·0	3180·9	3180·9
101·25	31·6	101·71	3210·1	207·0	3223·0	3223·1
115·63	23·2	115·80	3244·4	241·3	3264·6	3264·6
129·89	31·2	130·27	3283·5	280·4	3309·1	3308·6
144·96	38·2	145·68	3325·1	322·0	3357·6	3357·3
158·27	42·6	159·38	3361·6	358·5	3401·4	3401·9

These observations lead to the formula—

$$2955\cdot799 + 2\cdot413\ 165t + 0\cdot001\ 545\ 1t^2 + 0\cdot000\ 005\ 546\ 4t^3,$$

by means of which the calculated volumes in the last columns of the foregoing tables are obtained. It will be noticed that the divergences from the observed volumes are somewhat wider than usual, more particularly at the upper and lower temperatures, but the variations are scarcely sufficient to render it necessary to represent the expansion from 0° to the boiling point by more than one expression.

Dividing through by the first term and correcting for the expansion of the glass ($0\cdot0000247$), the formula becomes—

$$V = 1 + 0\cdot000\ 841\ 17t + 0\cdot000\ 000\ 542\ 892t^2 + 0\cdot000\ 000\ 001\ 889\ 3t^3,$$

by the aid of which the following table, showing the relative volumes of phosphorus tribromide at every 5^{Δ} between 0^{Δ} and 175^{Δ} has been calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	95	108643	495
5	100422	422	100	109143	500
10	100847	425	105	109649	506
15	101275	428	110	110161	512
20	101706	431	115	110679	518
25	102140	434	120	111202	523
30	102577	437	125	111731	529
35	103018	441	130	112266	535
40	103463	445	135	112807	541
45	103912	449	140	113357	549
50	104365	453	145	113913	556
55	104822	457	150	114476	563
60	105283	461	155	115046	570
65	105748	465	160	115622	576
70	106218	470	165	116205	583
75	106693	475	170	116796	591
80	107173	480	175	117395	599
85	107658	485	172·9	—	—
90	108148	490			

Pierre has also determined the expansion of phosphorus tribromide, and has expressed his observations by the two formulæ:—

$$\text{I. } V = 1 + 0\cdot000\ 847\ 20t + 0\cdot000\ 000\ 436\ 72t^2 + 0\cdot000\ 000\ 002\ 528t^3\ (0-100^\circ),$$

and

$$\text{II. } V = 1 + 0\cdot000\ 824\ 27t + 0\cdot000\ 000\ 914\ 31t^2 + 0\cdot000\ 000\ 000\ 055t^3\ (100-175^\circ),$$

which give results agreeing, on the whole, fairly well with those afforded by the single expression deduced from my observations—

	40°.	80°.	120°.	170°.
Pierre	103475	107187	111217	116682
Thorpe.....	103445	107164	111208	116832

Pierre remarks that phosphorus tribromide is characterised by an extremely regular rate of expansion—an observation fully borne out by my experiments.

Phosphoryl Chloride, POCl₃.

Prepared by heating an intimate mixture of phosphorus pentoxide and phosphorus pentachloride in the proportions required by the equation—

The product began to boil at 107°, the greater portion distilling over at about 107·5° (bar. 755·2°). As this boiling point is more than

a couple of degrees below that usually assigned to this compound, I solidified the chloride in a mixture of ice and salt, allowed it to melt partially and poured away the still liquid portion. This operation was repeated several times in the hope that any of the more volatile phosphorus trichloride which might be present would be removed. The boiling point was practically unaltered by this treatment; the liquid distilled completely between 107° and 107.5° , the greater portion boiling at 107.3° under a pressure of 751.0 mm.; $n = 0$; $t = 0$; corrected and reduced b. p. 107.23° .

A second sample, made by heating phosphorus pentachloride with crystallised boric acid, boiled at 107.4° under a pressure of 765.0 mm.; $t = 0$; $n = 0$; corrected and reduced b. p. 107.22° .

The first sample was analysed by breaking bulbs containing known weights of the chloride in a stoppered bottle partially filled with distilled water, and determining the amount of the chlorine in the solution.

Two determinations were made with the following results:—

	I.	II.
Weight of POCl_3 , <i>in vacuo</i> ..	1.3156 grams	1.4364 grams
Weight of AgCl ..	3.6907 "	4.1064 "
	I.	II.
Chlorine	69.37	69.39
		Calculated.
		69.36

Three determinations of specific gravity at 0° made with different bottles gave—

I	1.71185
II	1.71189
III	1.71182
Mean	1.71185

compared with water at the same temperature; compared with water at 4° the specific gravity is 1.71163.

Two series of observations with the dilatometers were made. The first with Dilatometer B gave in the water-bath—:

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	2911.6	2911.5	58.27	3101.9	3102.3
9.78	2941.5	2941.6	67.73	3137.0	3136.4
19.13	2971.1	2971.1	77.43	3172.3	3172.5
29.02	3003.1	3002.9	88.39	3214.9	3214.9
38.73	3035.1	3035.0	95.06	3241.8	3241.6
48.31	3067.1	3067.4			

In the oil-bath :—

T°.	t°.	TΔ.	V.	E.	Observed.	Calculated.
68·83	23·6	68·74	3127·3	225·8	3139·1	3139·0
88·33	25·9	88·54	3192·2	290·6	3213·7	3213·6
104·76	30·6	105·29	3250·5	348·9	3283·4	3283·9

These observations lead to the formula—

$$2911·47 + 3·057\ 81t + 0·002\ 674\ 9t^2 + 0·000\ 017\ 823t^3,$$

by means of which the numbers in the last column are calculated.

The second series made with Dilatometer C gave—

In the water-bath :—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	3017·8	3017·6	58·26	3215·4	3215·1
9·78	3048·8	3048·9	67·74	3251·7	3251·2
19·13	3079·4	3079·4	77·44	3288·5	3288·6
29·03	3112·7	3112·5	88·39	3332·4	3332·6
38·73	3146·2	3145·8	95·05	3360·6	3360·1
48·32	3179·1	3179·6			

In the oil-bath :—

T°.	t°.	TΔ.	V.	E.	Observed.	Calculated.
104·67	30·6	105·20	3370·3	344·7	3403·1	3403·4

These numbers afford the formula—

$$3017·63 + 3·167\ 52t + 0·003\ 051\ 3t^2 + 0·000\ 016\ 13t^3.$$

On dividing through by the first terms respectively, and correcting for the expansion of the glass, these formulæ become—

I. $V = 1 + 0·001\ 075\ 76t + 0·000\ 000\ 945\ 526t^2 + 0·000\ 000\ 006\ 145t^3$
and

II. $V = 1 + 0·001\ 074\ 37t + 0·000\ 001\ 037\ 09t^2 + 0·000\ 000\ 005\ 369t^3,$

The mean formula is—

$$V = 1 + 0·001\ 075\ 1t + 0·000\ 000\ 991\ 31t^2 + 0·000\ 000\ 005\ 757t^3,$$

by the aid of which the following table, showing the relative volume of phosphoryl trichloride at every 5° between 0° and 100°, is calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	60	106932	623
5	100540	540	65	107565	633
10	101086	546	70	108209	644
15	101637	551	75	108864	655
20	102194	557	80	109530	666
25	102758	564	85	110208	678
30	103330	572	90	110898	690
35	103909	579	95	111601	703
40	104496	587	100	112318	717
45	105092	596	105	113048	730
50	105696	604	110	113792	744
55	106309	613	107·23	1·133779	—

The indications of the dilatometers were further controlled by determining the weight of the phosphoryl chloride contained in a specific gravity bottle at 0° and at the temperature of steam from boiling water. The chloride employed was a different preparation from that used in the dilatometers: in fact, the two series of observations were made at an interval of several years with different balances, barometers, &c.; the determinations are therefore in every particular perfectly independent. The mean coefficient of expansion of the specific gravity bottle was found to be 0·00002633. Three observations were made with the following results: the weighings are reduced to a vacuum.

I at 0°	6·55751 grams	at $99\cdot96^\circ$ (bar. 759 mm.)	5·85339 grams
II „	6·55702 „	99·84 („ 755·5 „)	5·85320 „
III „	6·55708 „	99·74 („ 753·0 „)	5·8535 „

	Volume in ice.	Volume in steam.	Calculated from formula.
I	100000	at $99\cdot96$ 112292	112311
II	100000	99·84 112287	112296
III	100000	99·74 112281	112282

Considering that the determinations were made with different preparations at different times, and by perfectly distinct methods, the agreement is very satisfactory. The control is the more important in its relation to Matthiessen's remarks on the dilatometrical method of determining thermal expansions.

The specific gravity of phosphoryl trichloride at 10° , 51° , and at its boiling point, has already been determined by H. L. Buff.

The results of his observations, compared with mine for these 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 ($107\cdot23^\circ$).

Thiophosphoryl Chloride, PSCl₃.

Prepared by the action of phosphorus pentasulphide upon the pentachloride—

The materials were intimately mixed in the proportions required by this equation and heated in a sealed tube at a temperature of about 120°. The reaction is very regular, and large quantities of very pure thiochloride can be thus obtained. Occasionally the product has a slight yellow colour; if shaken with a little water, and dried by calcium chloride and distilled, it may be readily procured perfectly colourless. Thiophosphoryl chloride boils at 125·0° under a barometric pressure of 760·0 mm.

Corrected and reduced boiling point 125·07^A.

Two determinations of its specific gravity at 0°, compared with water at 0°, gave—

I	1·66815
II	1·66816
Mean	1·66816

A second preparation boiled constantly at 125·5°; $n = 0$; $t = 0$. Bar. 770·0 mm. Corrected and reduced boiling point 125·17^A. Mean boiling point 125·12^A. Two independent determinations made with bottles differing in capacity from those employed in the foregoing observations gave for the specific gravity of the second sample—

I	1·66868
II	1·66864 at 0°.

compared with water at 0^A. The mean sp. gr. at 0° compared with water at 4^A is 1·66820.

Other observations on record are:—

Mitscherlich	126—127°	
Baudrimont	124—125	1·631 at 22°.

The following observations of the rate of thermal expansion of this liquid were made in Dilatometer B in the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	2858·6	2858·4	45·39	2990·5	2990·8
11·33	2890·2	2890·4	56·62	3025·8	3025·6
22·42	2922·2	2922·3	68·10	3062·2	3062·3
34·26	2957·4	2957·2			

In the oil-bath :—

T°.	t°.	TA.	V.	E.	Observed.	Calculated
22·54	18·9	22·40	2922·1	35·5	2922·2	2922·2
34·55	20·3	34·42	2956·8	70·1	2957·7	2957·6
45·60	22·1	45·54	2989·0	102·4	2991·5	2991·2
62·39	23·8	62·27	3037·0	150·4	3043·0	3043·5
68·72	25·6	68·63	3056·6	170·0	3064·3	3064·1
79·78	27·3	79·83	3089·6	203·0	3101·0	3101·1
90·88	29·4	91·10	3123·5	236·9	3139·4	3139·5
102·16	31·9	102·65	3158·8	272·2	3180·1	3180·4
113·70	31·6	113·79	3193·0	306·4	3221·3	3221·3
124·12	34·1	124·88	3226·9	340·3	3262·1	3261·6

These observations lead to the formula—

$$I. 2858·375 + 2·797\ 16t + 0·002\ 088\ 15t^2 + 0·000\ 011\ 973t^3,$$

which affords the numbers seen in the last columns of the above tables.

A second series of observations made in Dilatometer C gave the following results. In the water-bath :—

A.	Observed.	Calculated.	A.	Observed.	Calculated.
0·00	2993·2	2992·7	45·39	3131·4	3131·7
11·33	3026·3	3026·4	56·63	3168·3	3168·2
22·41	3059·7	3059·9	68·10	3206·3	3206·4
34·27	3096·6	3096·6			

In the oil-bath :—

T°.	t°.	TA.	V.	E.	Observed.	Calculated.
22·54	18·9	22·40	3059·9	33·1	3060·0	3060·0
34·55	20·3	34·42	3096·2	69·5	3097·2	3097·1
45·61	22·1	45·55	3130·0	103·2	3132·4	3132·2
62·38	23·5	62·26	3180·3	153·6	3186·6	3186·8
68·74	25·6	68·65	3200·7	174·0	3208·7	3208·4
79·77	27·3	79·82	3235·0	208·3	3246·7	3246·9
90·91	29·4	91·13	3270·7	244·0	3287·1	3287·3
102·19	31·8	102·68	3307·7	281·0	3329·7	3330·2
113·71	31·6	113·80	3344·6	317·9	3372·9	3373·0
124·18	34·1	124·44	3379·3	352·6	3416·1	3415·7

From these numbers we obtain the formula—

$$II. 2992·730 + 2·957\ 39t + 0·001\ 591\ 39t^2 + 0·000\ 015\ 741\ 8t^3.$$

Dividing each formula through by its first term respectively, and correcting for the expansion of the glass, we obtain—

I. $V = 1 + 0.001\,004\,08t + 0.000\,000\,755\,491t^2 + 0.000\,000\,004\,208t^3$,
and

II. $V = 1 + 0.001\,012\,89t + 0.000\,000\,556\,160t^2 + 0.000\,000\,005\,273t^3$.

The mean formula is—

$V = 1 + 0.001\,008\,49t + 0.000\,000\,655\,82t^2 + 0.000\,000\,004\,745\,5t^3$,

by means of which the following table, showing the relative volumes of thiophosphoryl chloride at every 5° between 0° and its boiling point is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	70	107544	581
5	100505	505	75	108133	589
10	101015	510	80	108731	598
15	101529	514	85	109337	606
20	102047	518	90	109953	616
25	102570	523	95	110579	626
30	103097	527	100	111215	636
35	103630	533	105	111862	647
40	104169	539	110	112519	657
45	104714	545	115	113187	668
50	105266	552	120	113866	679
55	105824	558	125	114558	692
60	106390	566	125.12	1.145752	—
65	106963	573			

Phosphoryl Bromochloride, POBrCl₂.

I prepared this compound by means of the reaction by which it was first obtained by Menschutkin, *i.e.*, by the addition of bromine to ethoxyphosphorus chloride:—

80 grams of bromine were allowed to fall, drop by drop, into 74 grams of the chloride, which was kept well cooled and constantly shaken. The reaction, which is extremely violent, proceeds in strict accordance with the above equation: direct experiment showed that if the materials be well cooled and slowly mixed, the theoretical quantity of bromine is just needed to colour the liquid permanently orange. As the ethyl bromide boils at about 40° , and the bromochloride nearly 100° higher, the two liquids can be readily separated by distillation.

The bromochloride was found to boil constantly at 136.5° ; $t = 15^\circ$; $n = 1.08$. Bar. 760.5 mm. Corrected and reduced boiling point 137.6° .

It was analysed by breaking a bulb containing a known weight of the liquid beneath water, acidulating with nitric acid, and precipitating the hydrochloric and hydrobromic acids with silver nitrate.

Weight of bromochloride taken	0.9890 grams
Weight of mixed silver salts	2.3701 „
„ „ (calc.)	2.3720 „

2.3583 grams of the mixed silver salts, heated in a stream of dry chlorine, lost 0.2201 gram: whence we obtain—

	Found.	Calculated.
Bromine	40.05	40.30
Chlorine	35.74	35.83

Two determinations of the specific gravity of phosphoryl bromochloride gave—

I	2.1020 at 8.74 ^A
II	2.1011 at 9.17

compared with water at 4^A. At 0^A, compared with water at 4^A, the specific gravity becomes—

I	2.1206
II	2.1207
Mean	2.12065

Menschutkin found the boiling point 135–137°, and the specific gravity 2.059 at 0°.

The following observations of the rate of expansion of this substance were made in Dilatometer N.

In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
11.92	3375.8	3375.6	59.55	3539.7	3539.8
26.62	3424.9	3424.9	71.03	3582.2	3582.1
37.55	3462.8	3462.5	84.45	3632.8	3632.7
48.12	3499.2	3499.2			

In the oil-bath:—

T°.	t°.	T ^A .	V.	E.	Observed.	Calculated.
70.50	22.3	70.40	3574.4	100.6	3579.4	3579.2
84.35	26.1	84.41	3623.5	148.7	3632.6	3632.5
95.30	29.2	95.55	3661.8	188.0	3675.0	3675.1
134.15	36.2	134.55	3804.6	330.8	3841.3	3840.3

These results may be expressed by the formula—

$$3336.738 + 3.268\,830t + 0.001\,553\,32t^2 + 0.000\,014\,664t^3,$$

which affords the numbers seen in the last columns of the above tables.

Dividing through by the first term, and correcting for the expansion of the glass (0.00002553), this formula becomes—

$$V = 1 + 0.001\,005\,18t + 0.000\,000\,490\,530t^2 + 0.000\,000\,004\,406\,5t^3,$$

by the aid of which the following table showing the relative volume of phosphoryl bromochloride at every 5^Δ between 0^Δ and 140^Δ is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	75	108001	573
5	100503	503	80	108581	580
10	101010	507	85	109169	588
15	101520	510	90	109765	596
20	102034	514	95	110370	605
25	102551	517	100	110983	613
30	103072	521	105	111606	623
35	103597	525	110	112238	632
40	104128	531	115	112879	641
45	104663	535	120	113530	651
50	105204	541	125	114191	661
55	105750	546	130	114864	673
60	106303	553	135	115548	684
65	106862	559	140	116243	695
70	107428	566	137.7	1.15894	—

Ethoxyphosphorus Chloride, $\text{PCl}_2\cdot\text{C}_2\text{H}_5\text{O}$.

155 grams of carefully dehydrated alcohol were added, drop by drop, with constant shaking, to 460 grams of phosphorus chloride; these proportions being demanded by the equation—

The flask containing the chloride was surrounded by cold water and connected with an upright condenser. The mixture was allowed to stand for some time, and then submitted to distillation, and all coming over between 95° and 125° was collected separately. On rectification a large quantity of liquid was readily obtained boiling constantly at 117° to 118° .

A determination of the amount of chlorine in the liquid showed that it was practically pure.

1.1200 gram gave 2.2078 grams of silver chloride.

	Found.	Calculated.
Cl	48.58	48.26

The fraction employed in the determination of the specific gravity and rate of expansion, boiled at 117.8° ; $t = 0$; $n = 0$. Bar. 768.5 mm. Corrected and reduced boiling point 117.5° .

Two determinations of specific gravity gave—

I	1.30526
II	1.30527

at 0° compared with water at 4° .

The following observations of the rate of thermal expansion were made in Dilatometer E.

In the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
10.32	2895.8	2896.0	51.61	3028.8	3028.9
19.59	2924.7	2924.5	59.16	3054.6	3055.0
29.68	2956.5	2956.5	68.99	3089.8	3089.6
39.67	2989.0	2988.9	80.25	3130.6	3130.8

In the oil-bath :—

T° .	t° .	$T\Delta$.	V.	E.	Observed.	Calculated.
89.71	26.9	89.85	3152.3	179.1	3165.5	3166.0
97.72	30.3	97.99	3180.9	207.6	3197.6	3197.5
103.87	31.6	104.26	3202.2	229.0	3222.3	3221.9

These results lead to the formula—

$$2865.959 + 2.89462t + 0.00529388t^2 - 0.000002982t^3,$$

which affords the numbers seen in the last columns of the above tables.

Dividing through by the first term, and correcting for the expansion of the glass (0.00002303), this formula becomes—

$$V = 1 + 0.00102304t + 0.00000187367t^2 - 0.0000000061t^3,$$

by the aid of which the following table, showing the relative volume of ethoxyphosphorus chloride at every 5° between 0° and 120° , is calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	65	107425	625
5	100516	516	70	108058	633
10	101042	526	75	108701	643
15	101577	535	80	109352	651
20	102121	544	85	110012	660
25	102674	553	90	110681	669
30	103237	563	95	111358	677
35	103808	571	100	112043	685
40	104388	580	105	112737	694
45	104978	590	110	113439	703
50	105576	598	115	114150	711
55	106183	607	120	114869	719
60	106800	617	117.5	1.145087	—

Phosphenyl Chloride, C₆H₅.PCl₂.

I am indebted to Professor Michaelis, of Carlsruhe, the discoverer of phosphenyl chloride, for an extremely liberal supply of this remarkable and interesting compound. When received it was perfectly clear and transparent, but in course of time it had deposited a slight precipitate of free phosphorus.

Before distilling it was heated for some hours to 180—190° in a sealed tube. It boiled very constantly between 218.5° and 219.1°, the greater portion coming over at about 218.7°; $t = 20^\circ$; $n = 191$. Bar. 763.6 mm. Corrected and reduced boiling point 224.6°.

Its specific gravity was found to be 1.3428 at 0° compared with water at 4°.

Michaelis found the boiling point of phosphenyl chloride to be 222°, and its specific gravity 1.319 at 20°.

The following observations of its rate of expansion by heat were made in Dilatometer D.

In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
11.94	3261.2	3261.1	63.50	3399.6	3399.1
22.58	3289.1	3289.0	79.58	3444.2	3444.1
31.72	3313.0	3313.2	99.65	3502.6	3502.2
48.36	3358.4	3357.7			

In the oil-bath:—

T°.	t°.	TA.	V.	E.	Observed.	Calculated.
119·15	37·1	119·27	3551·6	167·6	3561·5	3561·5
131·17	39·1	131·48	3585·4	201·4	3600·0	3599·8
144·02	42·0	144·57	3622·4	238·4	3642·0	3642·2
In vapour of aniline		183·77	—	—	3778·8	3778·9

These numbers lead to the formula—

$$3230\cdot02 + 2\cdot598\ 6t + 0\cdot000\ 411\ 71t^2 + 0\cdot000\ 009\ 236\ 9t^3,$$

which affords the numbers given in the last columns of the above tables.

Dividing through by the first term and correcting for the expansion of the glass (0·0000213), this expression becomes—

$$V = 1 + 0\cdot000\ 825\ 8t + 0\cdot000\ 000\ 144\ 61t^2 + 0\cdot000\ 000\ 002\ 863t^3,$$

by the aid of which the following table, showing the relative volume of phosphenyl chloride at every 10° between 0° and 230°, is calculated :—

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	130	111609	996
10	100828	828	140	112631	1022
20	101660	832	150	113679	1048
30	102498	838	160	114756	1077
40	103345	847	170	115863	1107
50	104201	856	180	117003	1140
60	105069	868	190	118176	1173
70	105950	881	200	119385	1209
80	106846	896	210	120632	1247
90	107758	912	220	121916	1284
100	108689	931	230	123242	1326
110	109640	951			
120	110613	973	224·6	1·22522	—

Vanadyl Trichloride, VOCl₃.

Vanadium pentoxide was reduced to the trioxide by ignition in a stream of dry hydrogen, and the trioxide was heated in dry chlorine. I am indebted to Dr. Roscoe for the pentoxide: it was a portion of the sample employed by him in the determination of the atomic weight of vanadium, and had been prepared with great care: it was beautifully crystallised, and of a magnificent ruby-red colour when seen by transmitted light. The vanadyl trichloride was heated in a current of dry carbon dioxide for some time in order to free it from dissolved chlorine, and distilled into the flask in which its boiling point was to be

determined. It began to boil at 127.05° , the column rapidly rose to 127.15° , at which point it remained constant. $n = 10, t = 30^{\circ}$. Bar. 764.5 mm. Corrected and reduced boiling point, 127.19° .

Three determinations of specific gravity at 0° compared with water at 4° gave—

I	1.86550
II	1.86568
III	1.86557
Mean	1.86558

Compared with water at 4° , the specific gravity is 1.86534.

Roscoe observed that vanadyl trichloride boils at 126.7° , and had the specific gravity—

1.841 at 14.5°	= 1.8655 at 0°
1.836 „ 17.5	= 1.8653 „
1.828 „ 24.0	= 1.8665 „

I controlled the indications of the dilatometer by determining the amount 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:—

I. Weight of vanadyl trichloride at 10° *in vacuo* 7.15114 grams.

Ditto, after having been heated to 100.37° ,

bar. 770.3 mm. 6.66541 „

Expansion of glass for 1° 0.00002633

Hence 10,000 vols. at 0° become at 100.37° —

Observed 11090

Calculated 11091

II. Weight of vanadyl trichloride at 0° *in vacuo* 7.15156 grams.

Ditto, after having been heated to 100.10° ,

bar. 762.9 mm. 6.46736 „

Expansion of glass for 1° 0.00002633

Hence 10,000 vols. at 0° become at 100.10° —

Observed 11087

Calculated 11088

Observations of the rate of thermal expansion in Dilatometer C afforded the following results:—

In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2968·7	2968·7	35·09	3070·5	3070·3
11·38	3000·6	3000·8	45·85	3103·2	3103·1
22·73	3033·8	3033·6	56·99	3137·7	3137·9

In the oil-bath :—

T°.	t°.	T Δ .	V.	E.	Observed.	Calculated.
35·63	20·1	35·51	3070·7	44·0	3071·4	3071·5
46·73	21·7	46·71	3103·9	77·2	3105·8	3105·7
68·97	21·7	68·89	3169·7	143·0	3176·6	3176·4
80·16	24·1	80·32	3204·0	177·3	3214·3	3214·2
91·55	27·0	91·79	3239·5	212·7	3253·9	3254·1
102·92	29·4	103·40	3275·8	249·1	3295·6	3295·6
114·72	34·7	114·84	3312·3	285·6	3337·3	3337·8
124·81	37·2	125·06	3346·2	319·4	3377·4	3376·9

These numbers afford the formula—

$$2968.679 + 2.792\ 15t + 0.002\ 597\ 68t^2 + 0.000\ 009\ 410\ 76t^3,$$

which on dividing through by the first term and correcting for the expansion of the glass (0.0000247) becomes—

$$V = 1 + 0.000\ 965\ 236t + 0.000\ 000\ 898\ 260t^2 + 0.000\ 000\ 003\ 191\ 63t^3.$$

By the aid of this formula the following table has been calculated : it shows the relative volumes of vanadyl trichloride at every 5 Δ between 0 Δ and its boiling point.

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	70	107306	565
5	100485	485	75	107879	573
10	100975	490	80	108460	581
15	101469	494	85	109050	590
20	101969	500	90	109647	597
25	102474	505	95	110254	607
30	102985	511	100	110870	616
35	103502	517	105	111495	625
40	104025	523	110	112129	634
45	104555	530	115	112774	645
50	105091	536	120	113428	654
55	105634	543	125	114092	664
60	106184	550	130	114767	675
65	106741	557	127·19	1.143867	—

Arsenic Trifluoride, AsF₃.

Obtained by heating an intimate mixture of fluorspar and arsenious oxide with fuming oil of vitriol. An ordinary retort may be employed in the preparation, as the dry hydrofluoric acid simultaneously evolved has very little action on the glass. Large quantities of the fluoride may be readily prepared in this way, as much as 500 grams having been obtained in a single operation. On distillation the greater part of the liquid was found to boil constantly between 60.1° and 60.3° . $n = 0$, $t = 0$. Bar. 763.0 mm. Corrected and reduced boiling point, 60.4° .

In order to analyse it, a weighed portion of the fluoride was decomposed by water in a platinum dish, and after the addition of a few drops of hydrochloric acid, the arsenic was precipitated as sulphide.

0.4740 gram of fluoride gave 0.4415 gram of arsenic sulphide.

	Found.	Calculated.
Arsenic	56.85	56.91

Arsenic trifluoride is a heavy oily liquid, extremely volatile and readily decomposed by water with the formation of hydrochloric and arsenious acids. An admixture of a small quantity of water produces no turbidity: on adding excess, arsenious oxide gradually separates out in octohedra. Absolute alcohol and ether are miscible with the fluoride; chloroform is dissolved by it when hot, but separates out again on cooling. As arsenic trifluoride acts slowly upon glass, especially on flint glass, with the formation of silicon tetrafluoride, I determined its specific gravity and rate of expansion in a special apparatus, as I was unwilling to risk its action upon my dilatometers and specific gravity flasks.

Determination of specific gravity:—

Weight of bottle + AsF ₃ at 12.6° <i>in vacuo</i> ..	21.6417	grams.
" " + water.....	10.7765	"
" " (empty).....	4.0720	"

From these numbers we obtain 2.6206 as the sp. gr. of arsenic fluoride at 12.6° compared with water at the same temperature; at 0° compared with water at 4° it is 2.6659.

The rate of expansion was determined by ascertaining the weight of the fluoride required to fill the specific gravity bottle at various temperatures. The results must be considered as only approximate, as the glass was found to be slowly acted upon in the course of the observations, more particularly at the higher temperatures. The bottle was weighed from time to time during the observations, and

the results corrected for the slight loss of weight suffered by the glass.

Temp.	Observed.	Calculated.	Temp.	Observed.	Calculated.
0·0°	10000	10000	36·2°	10516	10517
5·8	10079	10082	42·2	10604	10603
12·5	10187	10178	49·7	10706	10711
20·0	10277	10284	59·8	10861	10859
28·7	10407	10409			

These results may be expressed with sufficient accuracy by the formula—

$$V = 1 + 0\cdot001\,418t + 0\cdot000\,000\,262t^2,$$

by means of which the numbers in the third column are calculated.

Assuming 0·000025 as the expansion-coefficient of the glass (soda-lime glass of German make), the above formula becomes—

$$V = 1 + 0\cdot001\,443t + 0\cdot000\,000\,297t^2,$$

by means of which the following table, showing the relative volumes of arsenic trifluoride at every 5° between 0° and 65°, is calculated. It will be seen that the rate of expansion although rapid is very uniform :—

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	10000	—	35	10509	73
5	10072	72	40	10582	73
10	10145	73	45	10655	73
15	10217	72	50	10729	74
20	10290	73	55	10803	74
25	10363	73	60	10876	73
30	10436	73	65	10951	75

Arsenic Trichloride, AsCl₃.

Prepared by heating arsenic trioxide in a stream of dry chlorine. The product was distilled upwards for some time in a current of dry carbon dioxide in order to remove dissolved chlorine. Care is necessary to exclude moisture, as the least trace of water renders the liquid turbid, owing to the formation of the oxychloride, As(OH)₂Cl.

On distillation the whole of the liquid was found to boil between 129·23° and 129·33°, the greater portion coming over at 129·30°. $n = 16$, $t = 15\cdot5$. Bar. 733·4 mm. Corrected and reduced boiling point 130·21°.

The specific gravity of the chloride was found to be 2·15761 at 8·08°, compared with water at the same temperature. At 0° it is 2·20500 compared with water at 4°: this number is almost identical with that found by Pierre, viz., 2·20495. According to Haagen, arsenic trichloride boils at 128° under a pressure of 754 mm., and has a specific gravity of 2·1668 at 20°: this reduced to 0° is 2·2067.

Observations of the rate of expansion made with Dilatometer C gave in the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2949·6	2949·7	23·34	3017·8	3017·7
8·01	2972·7	2972·7	35·31	3053·9	3053·8
11·62	2983·2	2983·2	47·10	3090·3	3090·2

In the oil-bath:—

T°.	t° .	T Δ .	V.	E.	Observed.	Calculated.
59·67	15·9	59·53	3123·5	136·8	3129·6	3129·8
70·35	12·9	70·33	3155·1	168·4	3165·2	3165·1
82·75	17·1	82·92	3193·0	206·4	3207·4	3207·4
94·26	22·7	94·61	3229·3	242·6	3248·0	3248·1
106·30	25·3	106·93	3266·9	280·3	3291·9	3292·3
117·50	26·2	117·69	3300·6	313·9	3332·4	3332·1
128·93	30·9	129·29	3338·3	348·6	3376·9	3376·5

These observations lead to the formula—

$$2949\cdot690 + 2\cdot851\ 284t + 0\cdot002\ 434\ 26t^2 + 0\cdot000\ 008\ 066\ 5t^3,$$

On dividing through by the first term and correcting for the expansion of the glass (0·0000247) this becomes—

$$V = 1 + 0\cdot000\ 991\ 338t + 0\cdot000\ 000\ 849\ 14t^2 + 0\cdot000\ 000\ 002\ 755\ 1t^3,$$

by means of which the following table, showing the relative volume of arsenic trichloride at every 5° between 0° and its boiling point, is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	70	107449	571
5	100498	498	75	108028	579
10	101000	502	80	108615	587
15	101507	507	85	109209	594
20	102019	512	90	109811	602
25	102536	517	95	110420	609
30	103058	522	100	111038	618
35	103586	528	105	111664	626
40	104119	533	110	112299	635
45	104658	539	115	112942	643
50	105203	545	120	113595	653
55	105755	552	125	114257	662
60	106313	558	130	114929	672
65	106878	565	130·21	1·14956	—

The thermal expansion of arsenic trichloride may be represented according to Pierre by the formula—

$$V = 1 + 0\cdot000\ 979\ 072\ 746t + 0\cdot000\ 000\ 966\ 948\ 200t^2 + 0\cdot000\ 000\ 001\ 777\ 204t^3,$$

which gives results uniformly lower than that 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

Thionyl Chloride, SOCl₂.

This substance is readily obtained by the action of sulphur dioxide upon phosphorus pentachloride. About 400 grams of the pentachloride were treated in successive portions of 100 grams with sulphur dioxide. The reaction begins even in the cold, and sufficient heat is generated during the process to bring about the speedy transformation of the materials into phosphoryl and thionyl chlorides :

By repeated fractionation the thionyl chloride was obtained boiling constantly between 77·2° and 78·2°, the greater portion of the liquid appearing to come over between 77·6° and 77·9°. $n = 18$, $t = 20$. Bar. 738·6 mm. Corrected and reduced boiling point, 78·8°.

Thionyl chloride when treated with water is decomposed in accordance with the equation—

Advantage was taken of this decomposition to determine the purity of the liquid by estimating the amount of sulphurous acid yielded by

a known weight of the substance. 0·3859 gram of the thionyl chloride was decomposed by water, the solution made up to about 600 c.c., and mixed with 50 c.c. of decinormal iodine solution (1 c.c. = ·012685 gram iodine), next a few c.c. of starch-paste, and a further addition of the iodine solution until the blue colour was persistent. In all 65·90 c.c. of the iodine solution were needed.

SO calculated .. 40·4 per cent. Found .. 40·8 per cent.

Two determinations gave for the specific gravity at 0°, compared with water at 4°:—

I	1·67672
II	1·67674
Mean	1·67673

According to Wurtz, thionyl chloride boils at 78°, and has a specific gravity of 1·675 at 0°. These numbers agree closely with those resulting from my own experiments.

A series of observations of the rate of the thermal expansion of thionyl chloride made in Dilatometer N, in the water-bath, afforded the following numbers:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
15·64	3418·9	3419·1	44·54	3537·4	3537·2
19·64	3435·0	3434·9	49·27	3557·8	3557·6
23·57	3450·6	3450·6	53·93	3577·5	3577·9
28·90	3472·0	3472·1	58·93	3600·0	3599·6
33·70	3491·8	3491·7	64·59	3626·0	3626·0
39·30	3515·0	3515·0	68·75	3645·4	3645·3

These numbers lead to the formula—

$$3358·587 + 3·814\,281t + 0·002\,972\,69t^2 + 0·000\,031\,954t^3,$$

by means of which the volumes in the last column of the above table are calculated.

Dividing through by the first term and correcting for the expansion of the glass (0·00002553), we obtain:—

$$V = 1 + 0·001\,164\,19t + 0·000\,000\,914\,18t^2 + 0·000\,000\,009\,536\,8t^3,$$

by the aid of which the following table, showing the relative volume of thionyl chloride at every 5° between 0° and 80°, is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	45	105511	647
5	100585	585	50	106169	658
10	101174	589	55	106838	669
15	101770	596	60	107520	682
20	102373	603	65	108215	695
25	102983	610	70	108924	709
30	103601	618	75	109648	724
35	104228	627	80	110387	739
40	104864	636	78·8	1·10208	—

Sulphothionyl Chloride, SSCl_2 .

About 500 grams of commercial sulphur chloride, which had been allowed to stand in contact with fragments of roll sulphur for some months, was distilled. It began to boil at about 135° , and a few drops of dark red liquid came over, after which the thermometer gradually rose to 139° , between which limits the whole of the chloride distilled. By repeated distillation, it was obtained of the constant boiling point $137\cdot62^\circ$; $n = 25$, $t = 18^\circ$. Bar. 761·2 mm. Corrected and reduced boiling point, $138\cdot12^\circ$.

A determination of specific gravity gave $1\cdot69802$ at $7\cdot58^\circ$, compared with water at the same temperature. At 0° , compared with water at 4° , this becomes $1\cdot70941$.

Other observations on record are:—

			Sp. gr.	
Dumas.....	138°	Bar?	$1\cdot687$	at?
Marchand	139	„	$1\cdot686$	„
Kopp	144	760 mm.	$1\cdot6802$	„ $16\cdot7^\circ$
			$1\cdot7055$	„ 0°
Haagen	$137\cdot7$	761·4 mm.	$1\cdot6828$	„ 20°

The following observations of the rate of thermal expansion of this liquid were made in Dilatometer C:—

In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2965·0	2964·7	37·16	3066·9	3067·1
12·51	2998·5	2998·6	49·08	3101·6	3101·3
24·74	3032·1	3032·2	62·13	3139·4	3139·5

In the oil-bath:—

T°.	t°.	TA.	V.	E.	Observed.	Calculated.
62·36	19·1	62·24	3133·7	147·5	3139·7	3139·8
74·77	23·2	74·79	3168·7	182·5	3177·8	3177·8
86·87	26·3	87·04	3203·5	217·3	3216·4	3216·1
100·59	29·1	101·09	3243·0	256·8	3261·3	3261·5
112·36	22·9	112·52	3273·6	287·4	3300·7	3299·9
124·83	29·6	125·17	3311·7	325·5	3343·6	3343·9
136·40	33·5	136·94	3347·0	360·8	3386·0	3386·5

These numbers lead to the formula—

$$2964.687 + 2.696\,519t + 0.001\,151\,35t^2 + 0.000\,012\,083\,8t^3,$$

which, on dividing through by the first term and correcting for the expansion of the glass (0.00002470), becomes

$$V = 1 + 0.000\,934\,25t + 0.000\,000\,410\,82t^2 + 0.000\,000\,004\,076\,9t^3,$$

The following table is calculated by means of this formula; it shows the relative volume of sulphothionyl chloride at every 5° between 0° and 140°:—

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	75	107410	529
5	100468	468	80	107946	536
10	100939	471	85	108488	542
15	101412	473	90	109038	550
20	101888	476	95	109596	558
25	102368	480	100	110160	564
30	102851	483	105	110733	573
35	103338	487	110	111315	582
40	103829	491	115	111907	592
45	104324	495	120	112507	600
50	104825	501	125	113116	609
55	105329	504	130	113735	616
60	105841	512	135	114364	629
65	106358	517	140	115003	639
70	106881	523	138·12	1.14571	—

The rate of expansion of this liquid has already been observed by Kopp, who has expressed his results by the formula—

$$V = 1 + 0.000\,959\,1t - 0.000\,000\,0381\,85t^2 + 0.000\,000\,007\,318\,6t^3.$$

This expression represents a slightly quicker rate than would be indicated by my observations, as the following comparison shows:—

	30°.	60°.	90°.	120°.
Kopp	10290	10590	10913	11271
Thorpe	10284	10583	10903	11251

Chlorosulphonic Acid, SO₂.OHCl.

I prepared this compound by the action of phosphoryl chloride upon concentrated sulphuric acid.

226 grams of phosphoryl chloride were mixed with 200 grams of the strongest oil of vitriol, and the mixture was gently heated and afterwards distilled. The greater portion of the liquid boiled between 153° and 154°, and, on redistillation, very nearly the whole came over between 153·3° and 153·6°, $n = 61$, $t = 27^\circ$. Bar. 745·6 mm. Corrected and reduced boiling point, 155·3^A.

The liquid was analysed by breaking a bulb containing a known quantity beneath the surface of water in a well-stoppered bottle, and determining the amount of soda needed for complete neutralisation.

Chlorosulphonic acid taken 0·9628 gram.

Caustic soda (NaHO) needed 0·9958 „

„ „ calculated 0·9917 „

Two determinations of specific gravity at 0°, compared with water at 4^A, gave:—

I 1·78465

II 1·78483

Mean 1·78474

According to Michaelis, chlorosulphonic acid boils at 158·4°, and has a specific gravity of 1·776 at 18°.

The following observations of its rate of expansion by heat were made in Dilatometer N in the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
10·93	3377·2	3377·7	64·42	3538·3	3538·5
25·34	3420·8	3420·5	73·90	3567·5	3567·9
36·64	3454·4	3454·2	89·05	3615·6	3615·7
48·51	3489·6	3489·9	100·05	3650·7	3651·1

These numbers afford the formula—

$$3345·551 + 2·942\ 465t + 0·000\ 321\ 819t^2 + 0·000\ 008\ 001\ 76t^3,$$

which, on dividing through by the first term and correcting for the expansion of the glass (0·00002553), becomes—

$$V = 1 + 0·000\ 905\ 05t + 0·000\ 000\ 118\ 647t^2 + 0·000\ 000\ 002\ 394\ 3t^3.$$

Assuming that this formula may be taken to represent the expansion of chlorosulphonic acid from 0° to its boiling point, the following table gives the relative volumes at every 5° between 0° and 160° :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	85	107926	487
5	100453	453	90	108416	490
10	100906	453	95	108910	494
15	101361	455	100	109409	499
20	101817	456	105	109911	502
25	102274	457	110	110418	507
30	102732	458	115	110929	511
35	103193	461	120	111445	516
40	103655	462	125	111966	521
45	104118	463	130	112492	526
50	104585	467	135	113024	532
55	105053	468	140	113560	536
60	105525	472	145	114103	543
65	105999	474	150	114651	548
70	106476	477	155	115205	554
75	106956	480	160	115765	560
80	107439	483	155.3	1.15238	—

Sulphuryl dichloride, SO₂Cl₂.

This substance was prepared by the very convenient method of Behrend, based on the decomposition of chlorosulphonic acid at a high temperature. When heated to about 200° for some hours, chlorosulphonic acid is almost completely resolved into sulphuryl dichloride and sulphuric acid; thus:—

The sulphuryl chloride is readily separated from the oil of vitriol by distillation. The product obtained from about 170 grams of the chlorosulphonic acid boiled with remarkable constancy at 69.1° , $n = 40$, $t = 25$. Bar. 750.5 mm. Corrected and reduced boiling point, 69.95° .

Two estimations of the specific gravity at 0° , compared with water at 4° , gave:—

I	1.70816
II	1.70812
Mean	1.70814

The following observations of the thermal expansion of this compound were made in Dilatometer E in the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
15·63	2909·9	2909·9	44·54	3017·0	3016·8
19·64	2924·3	2924·3	49·27	3035·6	3035·4
23·57	2938·4	2938·4	53·93	3053·8	3053·9
28·89	2957·8	2957·8	58·93	3074·3	3074·3
33·70	2975·8	2975·6	64·59	3098·0	3098·0
39·30	2996·7	2996·8	68·75	3115·9	3115·8

These numbers may be represented by the formula—

$$2855\cdot411 + 3\cdot448\ 264t + 0\cdot002\ 088\ 89t^2 + 0\cdot000\ 041\ 505t^3,$$

which, on dividing through by the first term, and correcting for the expansion of the glass (0·00002303), becomes—

$$V = 1 + 0\cdot001\ 230\ 65t + 0\cdot000\ 000\ 759\ 375t^2 + 0\cdot000\ 000\ 014\ 587t^3.$$

The following table, calculated by means of this formula, shows the relative volumes of sulphuryl dichloride at every 5^Δ between 0^Δ and 70^Δ :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	40	105138	675
5	100617	617	45	105825	687
10	101240	623	50	106526	701
15	101868	628	55	107241	715
20	102503	635	60	107973	732
25	103147	644	65	108720	747
30	103800	653	70	109487	767
35	104463	663	69·95	1·09479	—

Disulphuryl Chloride, S₂O₅Cl₂.

Made by the action of sulphur chloride upon sulphur trioxide. The product boiled almost completely between 135° and 138° , and on redistillation came over almost entirely between $138\cdot3^\circ$ and $138\cdot4^\circ$, the greater portion collecting at $138\cdot37^\circ$, $n = 48^\circ$, $t = 19\cdot3$. Bar. 758·8 Corrected and reduced boiling point $139\cdot59^\Delta$.

The liquid was analysed by decomposing a known weight with water and determining the amount of sodium hydrate needed for neutralisation.

Weight of disulphuryl chloride taken		1·3636 grams.
„ sodium hydrate needed		1·5212 „
„ „ „ calculated.....		1·5220 „

Two determinations of specific gravity were made at 0° —

I	1·85824
II	1·85868
Mean	1·85846

compared with water at 4°.

According to Michaelis this compound has a specific gravity of 1·819 at 18° and boils at 146°.

Observations of the rate of the thermal expansion of this liquid were made in Dilatometer E with the following results (the observations were made concurrently with those of chlorosulphonic acid):—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
10·93	2862·8	2863·0	64·42	3017·2	3017·3
25·34	2903·0	2902·9	73·90	3046·3	3046·5
36·64	2935·1	2935·1	89·05	3094·9	3094·6
48·51	2969·6	2969·6	100·05	3130·5	3130·6

These numbers afford the formula—

$$2833·444 + 2·678\ 383t + 0·002\ 395\ 19t^2 + 0·000\ 005\ 221\ 5t^3,$$

which gives results agreeing closely with those directly observed.

On dividing through by the first term and correcting for the expansion of the glass (0·00002303), this expression becomes—

$$V = 1 + 0·000\ 968\ 30t + 0·000\ 000\ 867\ 098t^2 + 0·000\ 000\ 018\ 623t^3.$$

By means of this formula the following table is calculated. It shows the relative volumes of disulphuryl chloride at every 5° from 0° to 140°, on the assumption that the formula is valid between these limits.

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	75	107829	562
5	100486	486	80	108397	568
10	100977	491	85	108971	574
15	101473	496	90	109553	582
20	101973	500	95	110141	588
25	102478	505	100	110736	595
30	102988	510	105	111339	603
35	103503	515	110	111948	609
40	104024	521	115	112565	617
45	104550	526	120	113190	625
50	105082	532	125	113822	632
55	105619	537	130	114463	641
60	106162	543	135	115111	648
65	106711	549	140	115767	656
70	107267	556	139·59	1·15713	—

Chromyl Dichloride, CrO₂Cl₂.

A large quantity of this liquid was prepared by the action of strong sulphuric acid upon a well-dried mixture of common salt and potassium dichromate. On distillation a perfectly clear product, free from the solid trichromyl dichloride, (CrO₂)₃Cl₂, was obtained; it boiled constantly at 115·77°. $n = 0^\circ$, $t = 0^\circ$. Bar. 757·7 mm. Corrected and reduced boiling point 115·9 Δ .

Its specific gravity was found to be 1·93540 at 14·48° compared with water at the same temperature; at 0° compared with water at 4 Δ it is 1·96101. In a former communication (*Chem. Soc. J.*, 1868) I have given the boiling point of chromyl dichloride as 116·8° and its specific gravity as 1·920 at 25° compared with water at the same temperature. This reduced to 0°, and compared with water at 4 Δ , becomes 1·9617.

The following observations of the thermal expansion of chromyl dichloride were made in Dilatometer D in the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	3322·6	3322·7	52·81	3497·4	3497·6
10·82	3356·9	3356·8	64·88	3541·2	3541·0
20·82	3389·1	3389·1	73·61	3573·4	3573·2
31·05	3422·9	3422·9	84·12	3612·8	3612·8
42·13	3460·5	3460·4	99·85	3674·3	3674·3

These results may be accurately represented by the formula—

$$3322\cdot658 + 3\cdot114\ 312t + 0\cdot003\ 501\ 27t^2 + 0\cdot000\ 005\ 812\ 7t^3,$$

which, on dividing through by the first term, and correcting for the expansion of the glass (0·0000213), becomes—

$$1 + 0\cdot000\ 958\ 60t + 0\cdot000\ 001\ 073\ 7t^2 + 0\cdot000\ 000\ 001\ 962t^3,$$

by means of which the following table, showing the relative volumes of chromyl dichloride at every 5 Δ between 0 Δ and its boiling point, is calculated:—

A.	Volume.	Diff.	A.	Volume.	Diff.
0	100000	—	70	107304	565
5	100482	482	75	107877	573
10	100969	487	80	108457	580
15	101463	494	85	109044	587
20	101962	499	90	109640	596
25	102466	504	95	110244	604
30	102978	512	100	110856	612
35	103495	517	105	111476	620
40	104019	524	110	112105	629
45	104549	530	115	112741	636
50	105086	537	120	113388	647
55	105630	544			
60	106181	551	115·9	1·12856	—
65	106739	558			

Carbon Bisulphide, CS₂.

The thermal expansion of [this liquid has already been studied by Muncke (*Ann. Chim. Phys.* [2], **64**, 5, 1837), Pierre, and Hirn, but their observations were necessarily made upon imperfectly purified material, as the method of obtaining carbon bisulphide free from the sulphuretted products which give it the extremely disagreeable smell which it ordinarily possesses, has only been discovered within the last few years. Although the amount of the foreign substances present in the particular specimens with which the observations above referred to were made was probably very small—too small, it may be, to materially affect the rate of expansion—it seemed advisable to repeat the determinations upon the properly purified liquid, on account of the special interest which attaches to a knowledge of the specific volume of this liquid.

About 500 grams of carefully rectified carbon bisulphide were digested with a large quantity of corrosive sublimate for 10 or 12 weeks. The liquid was next agitated with metallic mercury, distilled off white wax, digested with phosphoric pentoxide, and again distilled, care being taken to protect the liquid throughout the whole series of operations as much as possible from light (compare Herwig, *Pogg. Ann.*, **137**, 19 and 592). The bisulphide thus obtained was perfectly colourless, and possessed a faint aromatic odour, recalling that of chloroform. It boiled absolutely constantly at 45·95°, $n = 49^\circ$, $t = 17\cdot0^\circ$. Bar., 767·2. Corrected and reduced boiling point, 46·04°.

Two determinations of specific gravity at 0° compared with water at 0°, gave—

I		1·29233
II		1·29232

Compared with water at 4^A, the specific gravity is 1.29215.

Other observations on record are—

Gay-Lussac....	46.6	at 760 mm.	Sp. gr ..	1.2905	at 0°.
Regnault.....	46.20	„ 760 „			
Pierre.....	47.9	„ 755.8 mm.		1.2931	„ 0°.
Andrews.....	46.2	„ 769 „			
Buff.....	46.0	„ 760 „	1.30534 and	1.29182	at 0°.

Two series of observations of the expansion were made. With Dilatometer B in the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0.00	2890.6	2890.3	24.23	2971.7	2971.6
4.08	2903.6	2903.6	27.81	2984.4	2984.2
8.01	2916.6	2916.6	31.87	2998.7	2998.7
11.89	2929.5	2929.5	35.99	3013.9	3013.7
15.82	2942.6	2942.7	39.84	3027.9	3027.9
19.74	2956.5	2956.1	44.81	3046.9	3046.7

These numbers lead to the formula—

$$2890.300 + 3.25282t + 0.00312597t^2 + 0.000048714t^3.$$

The second series made in Dilatometer C gave—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0.00	3001.6	3001.4	24.23	3086.1	3086.0
4.08	3015.3	3015.3	27.81	3099.2	3099.1
8.01	3028.7	3028.7	61.87	3114.3	3114.2
11.89	3042.2	3042.1	35.99	3130.2	3129.8
15.82	3055.9	3055.9	39.84	3144.7	3144.6
19.74	3070.1	3069.8	44.81	3164.1	3164.3

numbers which afford the formula—

$$3001.420 + 3.378051t + 0.00328574t^2 + 0.000054151t^3.$$

On dividing through by the first terms and correcting for the expansion of the glass, these formulæ became respectively—

$$(I.) 1 + 0.00115093t + 0.00000110989t^2 + 0.000000016882t^3.$$

and

$$(II.) 1 + 0.00115019t + 0.00000112253t^2 + 0.000000018069t^3.$$

The mean formula is—

$$(III) V = 1 + 0.00115056t + 0.00000111621t^2 + 0.0000000174755t^3,$$

by the aid of which the following table, showing the relative volume of carbon bisulphide at every 5^Δ between 0^Δ and 50^Δ , is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	30	103599	626
5	100578	578	35	104238	639
10	101163	585	40	104892	654
15	101757	594	45	105563	671
20	102360	603	50	106250	687
25	102973	613	46·04	1·05704	—

The observations already referred to have yielded the following formulæ:—

$$\text{Muncke..... } 1 + 0\cdot001\,125\,691t + 0\cdot000\,001\,715\,049t^2 + 0\cdot000\,000\,001\,211\,66t^3$$

$$\text{Pierre } 1 + 0\cdot001\,139\,8t + 0\cdot000\,001\,370\,7t^2 + 0\cdot000\,000\,019\,123t^3$$

$$\text{Hirn } 1 + 0\cdot001\,168\,06t + 0\cdot000\,001\,649\,0t^2 - 0\cdot000\,000\,000\,811\,19t^3 + 0\cdot000\,000\,000\,060\,95t^4 \text{ (30° to 160°)}$$

My own results agree most closely with those of Pierre. Hirn's formula is, strictly speaking, only applicable to temperatures above the boiling point of carbon bisulphide. Muncke's observations are unquestionably too low.

	15°.	30°.	45°.
Muncke	101728	103535	105424
Hirn.....	101789	103650	105583
Pierre	101747	103594	105581
Thorpe.....	101744	103576	105536

III. DISCUSSION OF ERRORS.

The foregoing pages contain the results of observations made upon 47 liquids. Before proceeding to indicate and discuss the conclusions to which the investigation leads it may be desirable to collect together in synoptical form the numerical data upon which a discussion must depend. These data are embodied in the following tables.

Table I gives the several values of the coefficients in the expression—

$$V = 1 + at + bt^2 + ct^3,$$

representing the thermal expansions of the particular liquids investigated.

TABLE I.

Substance.	<i>a.</i>	<i>b.</i>	<i>c.</i>
Bromine	0·001 062 18	0·000 001 877 14	—0·000 000 003 085
Iodine monochloride..	0·000 915 90	0·000 000 832 96	0·000 000 002 750
Ethylene bromide	0·000 952 85	0·000 000 683 46	0·000 000 003 947
Ethylene chloriodide..	0·000 936 92	0·000 000 415 13	0·000 000 004 501
Ethylene chloride....	0·001 153 03	0·000 000 825 69	0·000 000 009 625
Ethidene chloride	0·001 284 02	0·000 001 890 62	0·000 000 007 848
Acetyl chloride	0·001 369 48	0·000 002 073 90	0·000 000 012 185
Trichloroacetyl chloride	0·001 091 13	0·000 000 272 05	0·000 000 008 293
Chloral	0·001 087 15	0·000 002 803 06	—0·000 000 016 040
Pentachlorethane	0·000 949 01	—0·000 000 074 50	0·000 000 005 280
Methene chloride	0·001 308 05	0·000 002 735 00	—0·000 000 001 330
Chloroform.....	0·001 230 24	0·000 001 713 80	0·000 000 008 338
Chloropierin	0·001 100 70	0·000 000 465 76	0·000 000 007 833
Carbon tetrachloride..	0·001 207 19	0·000 000 671 09	0·000 000 013 478
Bromoform.....	0·000 941 16	0·000 000 278 00	0·000 000 004 260
Trichlorobrommethane	0·001 082 31	0·000 000 655 82	0·000 000 005 858
Propionitrile	0·001 227 75	0·000 002 040 64	0·000 000 004 675
Epichlorhydrin	0·001 026 60	0·000 000 619 74	0·000 000 006 657
Allyl alcohol	0·000 993 71	0·000 000 599 86	0·000 000 012 285
Acetone	0·001 352 93	0·000 003 024 26	—0·000 000 000 290
Heptane	0·001 210 23	0·000 001 113 30	0·000 000 011 740
Ethyl-amyl	0·001 239 40	0·000 001 193 18	0·000 000 013 060
Octane.....	0·001 183 04	0·000 000 186 65	0·000 000 012 947
Di-isobutyl.....	0·001 197 01	0·000 000 621 22	0·000 000 014 166
Aniline	0·000 862 95	0·000 000 273 51	0·000 000 003 466
Picoline	0·000 966 53	0·000 000 845 90	0·000 000 004 567
Nitrogen tetroxide....	0·001 591	—0·000 003 970 15	0·000 000 215 3
Silicon tetrachloride ..	0·001 330 95	0·000 002 809 78	0·000 000 002 157
Titanium tetrachloride	0·000 982 61	0·000 000 505 53	0·000 000 005 131
Tin tetrachloride	0·001 160 55	0·000 000 646 17	0·000 000 007 727
Phosphorus trichloride	0·001 159 20	0·000 001 163 70	0·000 000 008 029
Phosphorus tribromide	0·000 841 17	0·000 000 542 89	0·000 000 001 889
Phosphoryl chloride ..	0·001 075 10	0·000 000 991 31	0·000 000 005 757
Thiophosphoryl chlo- ride	0·001 008 50	0·000 000 655 82	0·000 000 004 746
Phosphoryl bromo- chloride	0·001 005 20	0·000 000 490 53	0·000 000 004 407
Ethoxyphosphorus chloride	0·001 023 04	0·000 001 873 67	—0·000 000 000 610
Phosphenyl chloride ..	0·000 825 82	0·000 000 144 61	0·000 000 002 863
Vanadyl trichloride ..	0·000 965 24	0·000 000 898 26	0·000 000 003 192
Arsenic trifluoride....	0·001 443	0·000 000 297	—
Arsenic trichloride ..	0·000 991 34	0·000 000 849 14	0·000 000 002 755
Thionyl dichloride....	0·001 164 19	0·000 000 914 18	0·000 000 009 537
Sulphothionyl chloride	0·000 934 25	0·000 000 410 82	0·000 000 004 077
Chlorosulphonic acid..	0·000 905 05	0·000 000 118 65	0·000 000 002 394
Sulphuryl dichloride..	0·001 230 65	0·000 000 759 38	0·000 000 014 587
Disulphuryl chloride..	0·000 968 30	0·000 000 867 10	0·000 000 001 862
Chromyl dichloride ..	0·000 958 60	0·000 000 107 37	0·000 000 001 962
Carbon disulphide....	0·001 150 56	0·000 001 116 21	0·000 000 017 476

Table II shows the relative volumes of the several liquids at every 10° between 0° and their boiling points.

TABLE II.

$\Delta C.$	Bromine, Br.	Iodine monochloride, ICl.	Ethylene bromide, $C_2H_4Br_2$.	Ethylene chlor- iodide, C_2H_4ICl .	Ethylene chloride, $C_2H_4Cl_2$.	Ethylene chloride, $C_2H_4Cl_2$.	Ethylene chloride, $C_2H_4Cl_2$.	Acetyl chloride, C_2H_3OCl .	Trichloroacetyl chlo- ride, C_2OCl_4 .
0	100000	100000	100000	100000	100000	100000	100000	100000	100000
10	101081	100925	100960	100942	101162	101304	101391	101095	101095
20	102197	101867	101936	101894	102347	102650	102832	102200	102200
30	103347	102830	102931	102860	103559	104044	104328	103320	103320
40	104592	103815	103946	103843	104806	105489	105888	104461	104461
50	105742	104822	104984	104845	106092	106991	107518	105627	105627
60	106983	105855	106049	105868	107423	108554	—	106824	106824
70	—	106914	107140	106916	108806	—	—	108056	108056
80	—	108001	108262	107992	110246	—	—	109328	109328
90	—	109118	109417	109097	—	—	—	110645	110645
100	—	110267	110607	110234	—	—	—	112013	112013
110	—	—	111834	111408	—	—	—	113436	113436
120	—	—	113101	112619	—	—	—	114918	114918
130	—	—	114409	113871	—	—	—	—	—
140	—	—	—	115166	—	—	—	—	—

$\Delta C.$	Chloral, C_2Cl_3OH .	Pentachlorethane, C_2HCl_5 .	Methene chloride, CH_2Cl_2 .	Chloroform, $CHCl_3$.	Chloropicrin, $C(NO_2)_3$.	Carbon tetrachloride, CCl_4 .	Bromoform, $CHBr_3$.	Trichlorobromethane, CCl_3Br .
0	100000	100000	100000	100000	100000	100000	100000	100000
10	101114	100949	101335	101248	101106	101215	100944	101089
20	102274	101899	102724	102536	102226	102452	101897	102196
30	103470	102855	104167	103867	103365	103718	102868	103322
40	104694	103818	105662	105248	104528	105022	103837	104472
50	105936	104792	—	106684	105718	106372	104829	105649
60	107186	105781	—	108179	106941	107776	105839	106857
70	—	106788	—	—	108202	109241	106870	108098
80	—	107815	—	—	109505	110777	107925	109378
90	—	108866	—	—	110855	—	109006	110699
100	—	109944	—	—	112256	—	110116	112065
110	—	111052	—	—	113714	—	111256	—
120	—	112193	—	—	—	—	112430	—
130	—	113371	—	—	—	—	113641	—
140	—	114587	—	—	—	—	114890	—
150	—	115849	—	—	—	—	116180	—
160	—	117156	—	—	—	—	—	—

TABLE II (*continued*).

$\Delta C.$	Propionitrile, $C_3H_5CN.$	Epichlorhydrin, $C_3H_5OCl.$	Allyl alcohol, $C_3H_5OH.$	Acetone, $C_3H_6O.$	Heptane, $C_7H_{16}.$	Ethyl-amyI, $C_7H_{16}.$	Octane, $C_8H_{18}.$	Di-isobutyl, $C_8H_{18}.$
0	100000	100000	100000	100000	100000	100000	100000	100000
10	101249	101033	101026	101383	101222	101253	101186	101205
20	102541	102083	102072	102827	102474	102537	102384	102430
30	103879	103154	103145	104330	103763	103861	103601	103685
40	105267	104248	104252	105894	105094	105232	104845	104978
50	106707	105371	105402	107517	106476	106659	106124	106317
60	108202	106526	106601	109200	107916	108148	107445	107712
70	109755	107718	107857	—	109420	109709	108817	109169
80	111367	108950	109176	—	110995	111348	110247	110699
90	113044	110227	110568	—	112650	113070	111742	112309
100	114786	111551	112038	—	114390	—	113312	114008
110	—	112929	—	—	—	—	114963	115804
120	—	114362	—	—	—	—	116702	—

$\Delta C.$	Aniline, $C_6H_7N.$	Picoline, $C_6H_7N.$	Nitrogen tetroxide, $N_2O_4.$	Silicon tetrachlo- ride, $SiCl_4.$	Titanium tetrachlo- ride, $TiCl_4.$	Tin tetrachloride, $SnCl_4.$	Phosphorus trichlo- ride, $POCl_3.$	Phosphorus tribro- mide, $PBr_3.$
0	100000	100000	100000	100000	100000	100000	100000	100000
10	100866	100975	101573	101359	100988	101168	101172	100847
20	101740	101971	103196	102776	101990	102353	102371	101706
30	102623	102988	—	104252	103007	103561	103604	102577
40	103518	104031	—	105787	104044	104795	104874	103463
50	104426	105101	—	107384	105194	106061	106187	104365
60	105351	106202	—	109044	106188	107363	107547	105283
70	106294	107337	—	—	107302	108706	108960	106218
80	107256	108507	—	—	108447	110094	110429	107173
90	108241	109717	—	—	109627	111532	—	108148
100	109250	110968	—	—	110845	113024	—	109143
110	110285	112263	—	—	112103	114576	—	110161
120	111348	113606	—	—	113406	—	—	111202
130	112442	114998	—	—	114756	—	—	112266
140	113569	—	—	—	116155	—	—	113357
150	114729	—	—	—	—	—	—	114476
160	115927	—	—	—	—	—	—	115622
170	117163	—	—	—	—	—	—	116796
180	118441	—	—	—	—	—	—	—

TABLE II (*continued*).

$\Delta C.$	Phosphoryl chloride, $POCl_3$.	Thiophosphoryl chloride, $PSCl_3$.	Phosphoryl bromide, $POBrCl_2$.	Ethoxyphosphorus chloride, $POCl_2, C_2H_5O$.	Phosphenyl chloride, PCl_2, C_6H_5 .	Vanadyl chloride, $VOCl_3$.	Arsenic fluoride, AsF_3 .	Arsenic chloride, $AsCl_3$.
0	100000	100000	100000	100000	100000	100000	10000	100000
10	101086	101025	101010	101042	100828	100975	10145	101000
20	102194	102047	102034	102121	101660	101969	10290	102019
30	103330	103097	103072	103237	102498	102985	10436	103058
40	104496	104169	104128	104388	103345	104025	10582	104119
50	105696	105266	105204	105576	104201	105091	10729	105203
60	106932	106390	106303	106800	105069	106184	10876	106313
70	108209	107544	107428	108058	105950	107306	—	107449
80	109530	108731	108581	109352	106846	108460	—	108615
90	110898	109953	109765	110681	107758	109647	—	109811
100	112318	111215	110983	112043	108689	110870	—	111038
110	113792	112519	112238	113439	109640	112129	—	112299
120	—	113866	113530	114869	110613	113428	—	113595
130	—	—	114864	—	111609	114767	—	114929
140	—	—	116243	—	112631	—	—	—
150	—	—	—	—	113679	—	—	—
160	—	—	—	—	114756	—	—	—
170	—	—	—	—	115863	—	—	—
180	—	—	—	—	117003	—	—	—
190	—	—	—	—	118176	—	—	—
200	—	—	—	—	119385	—	—	—
210	—	—	—	—	120632	—	—	—
220	—	—	—	—	121916	—	—	—
230	—	—	—	—	123242	—	—	—

TABLE II (*continued*).

$\Delta C.$	Thionyl chloride, $SOCl_2$.	Sulphothionyl chlo- ride, $SSCl_2$.	Chlorosulphonic acid, SO_3HCl .	Sulphuryl dichlo- ride, SO_2Cl_2 .	Disulphuryl chlo- ride, $S_2O_5Cl_2$.	Chromyl dichloride, CrO_2Cl_2 .	Carbon bisulphide, CS_2 .
0	100000	100000	100000	100000	100000	100000	100000
10	101174	100939	100906	101240	100977	100969	101163
20	102373	101888	101817	102503	101973	101962	102360
30	103601	102851	102732	103800	102988	102978	103599
40	104864	103829	103655	105138	104024	104019	104892
50	106169	104825	104585	106526	105082	105086	106250
60	107520	105841	105525	107973	106162	106181	—
70	108924	106881	106476	109487	107267	107304	—
80	110387	107946	107439	—	108397	108457	—
90	—	109038	108416	—	109553	109640	—
100	—	110160	109409	—	110736	110856	—
110	—	111315	110418	—	111948	112105	—
120	—	112507	111445	—	113190	113388	—
130	—	113735	112492	—	114463	—	—
140	—	115003	113560	—	115767	—	—
150	—	—	114651	—	—	—	—
160	—	—	115765	—	—	—	—

Table III shows the formulæ and molecular weights of these bodies, their boiling points under the standard pressure, their relative volumes at this temperature (vol. at $0^\Delta = 1$), their specific gravities at 0° and at their respective boiling points, and lastly their specific volumes.

As the numerical value denoting the specific volume of a liquid depends upon the knowledge of its molecular weight and of its specific gravity at its boiling point under the standard pressure, or, what comes to the same thing, of its rate of thermal expansion, its point of ebullition, and its specific gravity at some other temperature, it is evident that this value, being founded on so wide an experimental basis, is liable to be affected with observational errors. It is desirable, therefore, in the outset, to trace the probable magnitude of these, and to indicate their effect upon the results, before we proceed to discuss their bearing on this question of the connection between the molecular weight of a body and its specific gravity when liquid.

1. *Errors of Atomic Weight.*—Of the 17 elementary bodies which enter into the composition of the material experimented upon in this investigation, the atomic weights of oxygen, chlorine, bromine, iodine, sulphur, nitrogen, and carbon are known with a very high degree of accuracy, certainly to within 0.05 of a unit. The atomic

TABLE III.

Substance.	Formula.	Mol. weight.	B. p. Δ.	Vol. at b. p.	Sp. gr. at 0°.	Sp. gr. at b. p.	Sp. vol.
Bromine	Br ₂	159·50	59·27	1·06911	3·18828	2·98218	53·48
Iodine monochloride	ICl	161·90	101·3	1·10419	3·18223	2·88196	56·18
Ethylene bromide	C ₂ H ₄ Br ₂	187·44	131·45	1·14602	2·21324	1·93124	97·06
Ethylene chloriodide	C ₂ H ₃ Cl	189·84	140·1	1·15179	2·16439	1·87915	101·03
Ethylene chloride	CH ₂ ClCH ₂ Cl	98·68	83·5	1·10764	1·28082	1·15635	85·34
Ethidene chloride	CH ₃ CHCl ₂	98·68	59·9	1·08538	1·20394	1·10923	88·96
Acetyl chloride	CH ₃ COCl	78·27	50·73	1·07640	1·13773	1·05698	74·05
Trichloroacetyl chloride	CCl ₃ COCl	181·38	118·0	1·14617	1·65640	1·44517	125·51
Chloral	CCl ₃ COH	147·01	97·2	1·11771	1·54480	1·3821	106·37
Pentachlorethane	CCl ₅ CHCl ₂	201·79	159·1	1·17008	1·70893	1·46052	138·2
Methene chloride	CH ₂ Cl ₂	84·71	41·6	1·05905	1·37776	1·30093	65·12
Chloroform	CHCl ₃	119·08	61·2	1·08362	1·52657	1·40877	84·53
Chloropierin	C(NO ₂)Cl ₃	164·01	111·9	1·13999	1·69225	1·48444	110·49
Carbon tetrachloride	CCl ₄	153·45	76·74	1·10268	1·63195	1·47999	103·68
Bromoform	CHBr ₃	252·22	151·2	1·16338	2·83413	2·43611	103·53
Trichlorobromomethane	CBrCl ₃	197·83	104·07	1·12634	2·05496	1·82446	108·43
Propionitrile	C ₃ H ₇ CN	54·92	97·08	1·14270	0·80101	0·70098	78·35
Epichlorhydrin	CH ₂ ClCH ₂ OCH ₂	92·24	116·55	1·13861	1·20313	1·05667	87·29
Allyl alcohol	CH ₂ CH ₂ CH ₂ OH	57·87	96·6	1·11529	0·86990	0·77998	74·19
Acetone	CH ₃ COCH ₃	57·87	56·53	0·81858	0·81858	0·75369	76·78
Heptane	CH ₃ (CH ₂) ₅ CH ₃	99·79	98·43	1·14111	0·70048	0·61386	162·56
Ethyl-amyI	(CH ₃) ₂ CH(CH ₂) ₃ CH ₃	99·79	90·3	1·13126	0·69692	0·61606	161·98
Octane	CH ₃ (CH ₂) ₆ CH ₃	113·76	125·46	1·17693	0·71883	0·61077	186·26
Di-isobutyl	(CH ₃) ₂ CH(CH ₂) ₂ CH(CH ₃) ₂	113·76	108·53	1·15534	0·71110	0·61549	184·83
Aniline	C ₆ H ₅ NH ₂	92·83	183·7	1·18924	1·03790	0·87274	106·37
Picoline	CH ₂ =C =	92·83	133·5	1·15497	0·96161	0·83258	111·50
Nitrogen tetroxide	N ₂ O ₄	92·06	21·6	1·03523	1·4903	1·43958	63·95
Silicon tetrachloride	SiCl ₄	169·48	57·57	1·08635	1·52408	1·40294	120·80
Titanium tetrachloride	TiCl ₄	189·48	136·4	1·15647	1·76041	1·52223	124·47

TABLE III (*continued*).

Substance.	Formula.	Mol. weight.	B. p. °.	Vol. at b. p.	Sp. gr. at 0°.	Sp. gr. at b. p.	Sp. vol.
Tin tetrachloride.....	SnCl ₄	259·28	113·9	1·15197	2·27875	1·97813	131·07
Phosphorus trichloride	PCl ₃	137·07	75·95	1·09827	1·61275	1·46845	93·34
Phosphorus tribromide	PBr ₃	270·21	172·9	1·17140	2·92311	2·49541	108·28
Phosphoryl chloride	POCl ₃	153·03	107·23	1·13378	1·71163	1·50967	101·37
Thiophosphoryl chloride.....	PSCl ₃	169·05	125·12	1·14575	1·66820	1·46599	116·11
Phosphoryl bromochloride.....	POBrCl ₂	197·41	137·6	1·15894	2·12065	1·83844	107·38
Ethoxyphosphorus chloride	POCl ₂ ·C ₂ H ₅ O	146·60	117·5	1·14509	1·80527	1·13989	128·61
Phosphenyl chloride	POCl ₂ ·C ₆ H ₅	178·52	224·6	1·2252	1·3428	1·10415	161·68
Vanadyl trichloride.....	VOCl ₃	173·27	127·19	1·14387	1·86534	1·63073	106·25
Arsenic trifluoride	AsF ₃	131·9	60·4	1·08824	2·6659	2·4497	53·84
Arsenic trichloride	AsCl ₃	181·0	130·21	1·14956	2·20500	1·91813	94·37
Thionyl dichloride	SOCl ₂	118·68	78·8	1·10208	1·67673	1·52143	78·01
Sulphothionyl chloride	SSCl ₂	134·70	138·12	1·14571	1·70941	1·49201	90·28
Chlorosulphonic acid	SO ₂ ·O·HCl	116·23	155·3	1·15238	1·78474	1·54874	75·05
Sulphuryl dichloride	SO ₂ Cl ₂	134·64	69·95	1·09479	1·70814	1·56025	86·29
Disulphuryl chloride	S ₂ O ₃ Cl ₂	214·50	139·59	1·15713	1·85846	1·60610	133·55
Chromyl dichloride.....	CrO ₂ Cl ₂	155·06	115·9	1·11560	1·96101	1·75780	88·21
Carbon disulphide	CS ₂	75·93	46·04	1·05704	1·29215	1·22242	62·11

weights of phosphorus, chromium, vanadium, arsenic and tin are probably known to within 0·2. The most doubtful members are titanium and antimony. Mendelejeff has already discussed the few determinations which have been made of the atomic weight of the former element, and he has concluded that the number hitherto assigned to it is probably too high by at least 2 units. An examination of the memoirs of Rose and Pierre, upon whose determinations the commonly accepted value of Ti depends, will serve to show that Mendelejeff's doubts are sufficiently well founded to render a fresh investigation on this subject very desirable. I have been induced to attack this question, as much for the sake of testing Mendelejeff's hypothesis as to the place of titanium in the system of the chemical elements, as for the knowledge which it is calculated to afford of the particular numerical value to be assigned to this metal. The investigation has proved more tedious than was anticipated, owing to the difficulty of finding a compound fulfilling all the conditions to be desired in a substance which is to serve for an atomic weight determination. I have therefore provisionally adopted Rose's number as modified by Mendelejeff. That considerations of the kind adduced by the Russian chemist in this particular instance ought to be accepted with caution is indicated by the analogous case of tellurium, which, according to Mendelejeff's classification, ought to be placed between iodine and antimony with an atomic weight of 125, whereas all experimental evidence goes to show that this value is too low by at least 2 units. The recent observations of Mr. W. L. Wills have proved that the atomic weight of tellurium is certainly not lower than 126·8, and is probably as high as 127·8, thus confirming the determinations of Berzelius and of von Hauer.

It seems highly probable that the number generally assigned to Sb, on the authority of Dumas and of Dexter, is too high by about 2 units. The value adopted by me is that recently determined by Professor J. P. Cooke, of Harvard, from a large and extremely concordant series of observations, made with various antimonial compounds. This value (120·0) agrees almost exactly with that found by Schneider, in 1856.

2. *Errors of Specific Gravity.*—These may be of two kinds: we may have in the case of a perfectly pure liquid errors of weighing, or in the determination of the temperature; or we may have in addition the effect of impurities in the compound. A careful revision of my observations leads me to conclude that the errors from the first named causes rarely exceed 1 in 10,000. And when regard is had to the very high degree of purity of the greater number of the liquids experimented upon, I am disposed to believe that the value given represents the true specific gravity in the great majority of cases to within 0·1 per cent.

As a rule the inorganic compounds could be readily obtained pure. Preparations of phosphoryl chloride, for example, whether made by the action of oxalic acid or of boric acid upon the pentachloride, or by heating this substance with the pentoxide, had identical specific gravities. This is, of course, not equally true of bodies separated by fractional distillation, but with due care and by operating on large quantities, the effect of possible admixture becomes extremely small; as an instance I may refer to the case of ethidene chloride given on p. 186; two samples of this liquid, obtained by distinctly different methods, one of which necessitated long continued fractionation, afforded results which differed by only 0.08 per cent. The observations, as it happened, were absolutely independent; they were made in both cases in duplicate, with different bottles, thermometers, balances, and weights.

3. *Errors in the Determination of the Thermal Expansion.*—I have already sought to prove by direct experiment that the dilatometrical method of determining the expansion of a liquid is calculated to afford a trustworthy result. The observations on water, given on p. 171, were undertaken expressly to test this point. The indications of the dilatometer depend, of course, upon several observational magnitudes, but I am unable to discover any evidence for the existence of any constant errors which would exert a preponderating influence in a special direction. A properly calibrated dilatometer, of which the rate of expansion is known, will afford results identical with those furnished by absolutely independent methods, such as that of displacement, as employed by Hagen and by Matthiessen. I have also sought to show that the method of correcting for the cooled portion of the liquid contained in the stem introduces no sensible error in the result; the observations obtained in the water-bath, when the whole of the liquid was of uniform temperature, are practically identical with those afforded by the oil-bath as corrected, where a considerable portion of the liquid in the stem possessed a much lower temperature than that in the bulb.

The discrepancy in my own determinations of the relative volume of a liquid at any temperature between 0° and its boiling point may be set down as 1 in 10,000. That two preparations of the same liquid, even when obtained by perfectly independent methods, do actually show identical rates of thermal expansion may be seen from the example, already quoted, of ethidene chloride, given on p. 186. Additional instances might be adduced in the cases of phosphoryl and thiophosphoryl chlorides, and of iodine monochloride.

4. *Errors in the Determination of the Boiling Point.*—I have already detailed the precautions which I adopted to ascertain the boiling points of the liquids experimented upon. All the known sources of error,

such as overheating, succussion, &c., were carefully guarded against. The reduction to the standard pressure is, of course, arbitrary, inasmuch as it assumes the validity of Dalton's law, but the error thereby introduced may be neglected, on account of the small range of barometric pressure; the boiling points are certainly more nearly comparable than they would have been had no such correction been applied. There is one possible source of error, of which so far as I know, no heed has yet been taken in determinations of this character, and that is, the influence of radiation. Lothar Meyer has already directed attention to this point, but experimental evidence as to the magnitude of its action is altogether wanting. I find that a thermometer, of which the bulb is surrounded by black cloth or caoutchouc tubing, when placed in steam, invariably reads a few tenths of a degree higher than when the bulb is in immediate contact with the vapour, but my observations are at present too few in number to enable me to state to what this phenomenon is actually due. I think, however, that it can hardly be attributed to pressure on the bulb.

In the absence of proper data it is impossible to give any precise estimate of the amount of error which may affect the determinations of the boiling points of the liquids. When it is borne in mind that nearly all the bodies were of comparatively low boiling point (40 out of the 47 liquids boiling between 46° and 140°), and that the majority of these could readily be obtained of a high degree of chemical purity, I should suppose that the determinations cannot be affected with an error so considerable as 1° . Let us assume, however, that such an error was possible, and on the basis of this and of the former estimations, let us seek to determine the effect of these errors on the determination of the specific volume.

Let σ be the specific volume, W the molecular weight, and s the specific gravity of the substance at the boiling point. Then—

$$\sigma = \frac{W}{s}.$$

If further S_0 be the specific gravity at 0° , and V_0 and V be the volumes at 0° and at the boiling point respectively, the above relations may be written—

$$\sigma = \frac{WV}{S_0 V_0} \text{ or } \frac{WV}{S_0} \text{ if } V_0 = 1.$$

Hence if $\delta\sigma$ be the error in σ , and a similar notation be used for the other quantities, and if we suppose all the errors to be of such sign that they tend to alter the value of σ in the same direction, then—

$$\delta\sigma = \frac{\delta W}{S} + \sigma \left\{ \frac{\delta S_0}{S_0} + \frac{\delta V}{V} \right\}.$$

δV consists of two parts, the first depending on the inaccuracy in

the knowledge of the law of expansion; the second on that of the determination of the boiling point. If α be the coefficient of expansion of the substance at the boiling point t , we may put

$$\delta V = \delta \sigma + \alpha \delta t.$$

If, further, we assume that for all the liquids $\delta S_0 = \cdot 001$ and $\delta V = \cdot 0001$, then—

$$\delta \sigma = \frac{\delta W}{S} + \frac{\sigma}{1000} \left\{ \frac{1}{S_0} + \frac{1}{10V} \right\} + \frac{\sigma \alpha \delta t}{V}.$$

Taking the estimations given on pp. 372 and 373 for the errors of atomic weight, I have calculated the effect on the determination of the specific volume in the cases of a number of the liquids, and in no instance does it amount to a unit.

Thus in the case of bromine—

$$\delta \sigma = \frac{\cdot 1}{3} + \cdot 053 \left\{ \frac{1}{3} + \frac{1}{10 \cdot 7} \right\} + \frac{53 \times \cdot 00116}{1 \cdot 07} = 0 \cdot 11.$$

In that of chloropicrin—

$$\delta \sigma = \frac{\cdot 35}{1 \cdot 5} + \cdot 110 \left\{ \frac{1}{1 \cdot 7} + \frac{1}{11 \cdot 4} \right\} + \frac{110 \times \cdot 00124}{1 \cdot 14} = 0 \cdot 42.$$

In the case of phosphorus trichloride—

$$\delta \sigma = \frac{\cdot 35}{1 \cdot 5} + \cdot 093 \left\{ \frac{1}{1 \cdot 6} + \frac{1}{11 \cdot 0} \right\} + \frac{76 \times \cdot 0013}{1 \cdot 1} = 0 \cdot 39.$$

In that of phosphoryl monochloride—

$$\delta \sigma = \frac{\cdot 4}{1 \cdot 8} + \cdot 107 \left\{ \frac{1}{2 \cdot 1} + \frac{1}{11 \cdot 6} \right\} + \frac{107 \times \cdot 00116}{1 \cdot 16} = 0 \cdot 39.$$

It will be seen that the uncertainty respecting the molecular weight of the compound has usually the greatest effect upon the value for the specific volume.

In the case of isomeric compounds the specific volumes of which are to be compared together, it is unnecessary to take into account the possible errors of atomic weight. It may be shown that the observed difference, for example, between ethidene chloride and ethylene chloride is considerably greater than can be accounted for by experimental errors.

But whatever may be the final effect of the various errors incidental to this method of determining the specific volume of a liquid substance, it is certain that the results are sufficiently precise to permit of trustworthy conclusions being drawn as to the connection between the specific gravity of such bodies and their molecular weights and chemical constitution. One proof of this is afforded by the fact that

different observers working by independent, and in some cases very dissimilar methods, and upon substances of very different origin, have obtained substantially identical results. It will have been noticed in the course of the paper, that the specific gravities, boiling points, and rates of thermal expansion of a certain number of the liquids which have served me for purposes of comparison, have already been determined, more particularly by Pierre and Kopp. I have calculated from the data furnished by their observations, the specific volumes of these liquids, assuming for their molecular weights the numbers given in Table III.

I will first compare my results with those of Pierre; these it will be observed mainly refer to inorganic substances, and more particularly to combinations containing chlorine and bromine.

	Specific volume.	
	Pierre.	Thorpe.
Bromine.....	53·72	53·48
Phosphorus bromide	108·35	108·28
Silicon tetrachloride.....	121·48	120·80
Titanium chloride.....	124·32	124·47
Tin tetrachloride	132·03	131·07
Phosphorus chloride.....	93·48	93·34
Arsenic chloride	94·61	94·37
Carbon bisulphide.....	62·23	62·11

It will be noticed that the agreement is remarkably close; the difference in the extreme case (that of tin tetrachloride) is about 0·7 per cent., and in mean it is only about 0·2 per cent. As a rule Pierre's numbers are slightly greater than mine; this is probably due to the circumstance that his determinations of boiling points are usually higher, owing to the fact of the thermometer bulb being placed in the heated liquid, and not in its vapour. This would tend to give a lower number for the specific gravity at the boiling point, and therefore a higher value for the specific volume.

Of the organic compounds investigated by Pierre, the following also serve for comparison with my results:—

	Specific volume.	
	Pierre.	Thorpe.
Ethylene chloride.....	85·45	85·34
Ethylene bromide.....	97·70	97·06
Chloroform	84·63	84·53
Carbon tetrachloride	103·98	103·68

In all the above instances Pierre's numbers are slightly in excess of

mine, but the extreme difference is not greater than in the former series, and on the average is less than 0·3 per cent.

Comparatively few of the large number of substances investigated by Kopp are available for the purpose of direct comparison with the results of my observations. The following, however, may be quoted:—

	Specific volume.	
	Kopp.*	Thorpe.
Acetyl chloride	74·95	74·05
Acetone	77·09	76·78
Aniline	105·99	106·37
Di-isobutyl	184·50	184·83

The greatest difference here (1·2 per cent.) is in the case of acetyl chloride, and this is mainly attributable to the higher boiling point (55—56°) and lower specific gravity observed by Kopp, due probably to a slight admixture of acetic anhydride, which seems to be invariably formed in the preparation of this compound by Gerhardt's method.

Buff, in the course of the observations made to test his hypothesis as to the connection between the specific volume of an element, and its atomic value (*Ann. Chem. Pharm.*, Suppl. 4, 129), determined the specific gravity of phosphorus and phosphoryl chlorides at various temperatures. His observations at the boiling points of these liquids furnish results which are almost identical with mine.

	Specific volume.	
	Buff.	Thorpe.
Phosphorus chloride	93·33	93·34
Phosphoryl chloride	101·41	101·37

IV. CONCLUSIONS.

Having thus, I hope, succeeded in proving that the numbers contained in the last column of Table III may be legitimately considered as denoting with approximate accuracy the specific volumes of the respective liquids, I proceed to indicate the conclusions which may be based upon them.

1. I cannot regard it as absolutely proved that isomeric liquids of the same chemical type, using that phrase in the sense in which Kopp employs it, have invariably the same specific volume. It is certain, for example, that ethidene chloride and Dutch liquid have not the

* Kopp's specific gravities are referred to water at 0°, instead of at 4°. The effect of this difference is, however, unimportant.

same specific gravity at their boiling points, and accordingly have not the same specific volume. The observations have given for—

	Specific gravity at boiling point.	Specific volume.
Ethylene chloride.....	1.15635	85.34
Ethidene chloride.....	1.10923	88.96
		<hr/>
	Difference..	3.62

This difference of 3.62 cannot be fairly attributed to errors of observation. The agreement of my observations with those of Pierre in the case of ethylene chloride, and the very concordant results obtained from the two independent series made with ethidene chloride, seem to me to leave no room for doubt on this point.

The specific volumes of ethylene chloride and of its analogues, $\text{C}_2\text{H}_4\text{Br}_2$ and $\text{C}_2\text{H}_4\text{ICl}$, are considerably below the numbers calculated by means of Kopp's values.

	Observed.	Calculated.	Diff.
Ethylene chloride	85.3	89.5	4.2
„ bromide....	97.1	99.5	2.4
„ chloriodide..	101.0	104.2	3.2

The experimental evidence, so far as it goes, seems to show that the normal hydrocarbons have a lower specific gravity at their boiling points, and hence have a greater specific volume than their isomerides. But this evidence at present hardly goes far enough to permit of a definite conclusion: we require a much larger number of observations made upon hydrocarbons of different homologous series. Unfortunately, however, these bodies are very difficult to obtain pure.

The mean difference between the specific volume of heptane and octane, and of ethyl-amyl and di-isobutyl is (including Kopp's number for the latter substance) 22.7, which is very near the mean value given by Kopp, viz., 22, for an increment of CH_2 .

It is, of course, quite possible that the specific volumes of carbon and hydrogen may be slightly modified by the mode in which the atoms are grouped in a compound: that we may have, in fact, variations of a kind similar to that which Gladstone, and, more recently, Brühl have shown to exist in the atomic refraction of carbon, dependent on the manner of its combination. Indeed it is not improbable that an intimate connection exists between the refractive power of such compounds and their specific volumes. Landolt has inferred that differences of molecular grouping in no way affect the refractive index of the constituent atoms, and Gladstone has shown that as a general law the molecular refractive power of a body is equal to the sum of the refraction of the atoms, just as it has been inferred that the

specific volume of carbon is invariable, and that the specific volume of a compound liquid is equal to the sum of the specific volumes of its constituent elements or compound radicles. Exceptions, however, are known to this law: thus the molecular refraction of many benzene derivatives, ethereal oils, and terpenes, and other bodies relatively rich in carbon is considerably greater than that calculated from their atomic refractions. Brühl has succeeded in detecting the relation between the constitution of these bodies and their optical character: he has shown that their refractive power depends upon the mode of combination of the constituent atoms; it appears, for example, that in the case of unsaturated bodies the atoms, which are more than once directly united to each other, exert a greater influence in propagating light than atoms which with the same atomic value are united to other atoms. Gladstone has pointed out that isomeric bodies occasionally differ widely in their optical properties: thus aniline and picoline, each C_6H_7N , have totally different refraction equivalents. It is also certain that they have totally distinct specific volumes, thus:

	Aniline.	Picoline.
Kopp	106.0	—
Thorpe	106.4	111.5

It may be further noted that a large number of those bodies, of which the molecular refraction is greater than the computed value, have also a specific volume considerably less than the calculated numbers. The specific gravity, boiling point, and rate of thermal expansion of benzene are known with great accuracy from the experiments of Kopp (*Jahresb.*, 1847-8, 65); Louguinine (*Jahresb.*, 1867, 48); Pisati and Paternò (*Chem. Soc. J.* [2], **12**, 686); and Adrieenz (*Ber.*, **6**, 442); and from their observations I have calculated the specific volume of this liquid with the following results:—

Kopp	95.94
Louguinine.....	95.98
Pisati and Paternò	95.94
Adrieenz.....	95.90
	<hr/>
Mean	95.94
Calculated specific volume ..	99.0

The observed values it will be noticed are extremely concordant, but they differ by more than 3 per cent. from the computed value. Differences of the same order are exhibited by a number of aromatic compounds; I select the following from Kopp's observations:—

	Specific volume.		Difference between observed and computed.
	Observed.	Computed.	
Phenol.....	103·6	106·8	+ 3·2
Benzyl alcohol	123·7	128·8	+ 5·1
Benzoic acid	126·9	130·0	+ 3·1
Benzyl aldehyde....	118·4	122·2	+ 3·8
Cymene	183·5	187·0	+ 3·5
Naphthalin.....	149·2	154·0	+ 4·8

It might certainly be inferred from these observations that CH_2 has a different value in the benzene derivatives from that which it possesses in organic compounds generally.

Our views as to the constitution of the aromatic compounds would lead us to expect that the specific volume of benzene (and the derivative in which the benzene group functions) would in all probability be different from that deduced from observations made for the most part on compounds of totally different constitution. Kopp (*Ann. Chem. Pharm.*, Supp. 5, 303) has shown from Louguine's observations, that, whilst benzene has an abnormally low specific volume, its homologues show the constant increase of 22 in the volume for an increment of CH_2 , which is what might be anticipated, since these bodies are produced by the addition (substitution) of methyl, ethyl, &c., to the benzene group.*

Indeed other values have been calculated for carbon and hydrogen: Lothar Meyer makes $\text{H} = 3$, and Loschmidt $\text{C} = 14$ and $\text{H} = 3\cdot5$, and by assuming that half the carbon atoms in benzene have the value 11, and the remainder the value 14, and that hydrogen has the constant value $3\cdot5$, we obtain a calculated value for this hydrocarbon which is identical with the observed number: $(11 \times 3) + (14 \times 3)$ $(3\cdot5 \times 6) = 96\cdot0$.

It would be interesting to determine how far such a dissimilarity in the specific volumes of the carbon atoms, or of the CH groups in benzene, is in harmony with the dynamical conceptions of the constitution of this hydrocarbon which we owe to Kekulé and to Ladenburg.

* I may be allowed to quote the following from Oscar Meyer's *Die Kinetische Theorie der Gase*:— . . die Form der Molekel und die Gruppierung der atome in derselben kann Einfluss auf den in Minimum erforderlichen Raum haben. Ein platte Molekel mit nahezu in einer Ebene neben einander gelagerten Atomen wird wenn die bei ihren, von der Wärme veranlassten Bewegungen sich dreht, mehr Raum beanspruchen, als eine Kugelförmige Molekel mit enger zusammengedrängten Atomen. So ist es . . . leicht erklärlich, dass den Atomen je nach ihrer Stellung in der Molekel eine verschiedene Raumerfüllung zugeschrieben werden darf. Art. Molecular-Volumen, p. 218.

I would also here recall to mind Jungfleisch's observations on the specific volumes of the chlorine substitution products of benzene. From these it is evident that the positions of the chlorine atoms affect in a very marked manner the specific volume of the product. (*Compt. rend.*, **64**, 911).

The only aromatic compounds contained in the table given on p. 144 are aniline and the phosphenyl chloride of Michaelis. The probable specific volume of the former liquid cannot be very accurately computed on account of the uncertainty which attaches to the particular value of the nitrogen atom in this compound. I found the specific volume of aniline to be 106·4, which is identical with Kopp's determination, but it happens that this very number was employed by Kopp to calculate the probable value of N in this class of compounds.

Phosphenyl chloride, $\text{PCl}_2\cdot\text{C}_6\text{H}_5$, however, resembles the other aromatic compounds in possessing a lower specific volume than the computed value.

Observed sp. vol. $\text{PCl}_2\cdot\text{C}_6\text{H}_5$	161·7
Calculated $(25·3 + 45·4 + 66 + 27·5) =$	164·2
	<hr/>
Difference ..	2·5

The estimated values of P and Cl are those given on pp. 384 and 387, those for C and H are due to Kopp.

2. My observations furnish additional evidence in support of the assumption already regarded by Kopp and others as highly probable that an element or a compound radicle occupies the same volume in combination as in the free state. I find, by direct observation, that the specific volume of nitrogen tetroxide is 64, hence $\text{NO}_2 = 32$. The specific volume of chloroform is 84·5 : that of chloropierin is 110·5. Chloropierin may be regarded as derived from chloroform by the substitution of an atom of hydrogen by an equivalent amount of NO_2 .

Hence we have—

Specific volume $\text{C}(\text{NO}_2)\text{Cl}_3$	110·5
„ CHCl_3	84·5
	<hr/>
	26·0
Add specific volume of H	5·5
	<hr/>
Calculated volume of NO_2	= 31·5
Observed „ „	32·0

Similar evidence is afforded by ethylene bromide and ethylene chloriodide. If we deduct the specific volume of C_2H_4 , calculated by means of Kopp's values, from the observed specific volumes of ethylene bromide and ethylene chloriodide, we obtain numbers which are

nearly equal to the specific volumes of bromine and of iodine monochloride as determined by experiment.

		Sp. vol. Br.	
		Calculated.	Observed (mean).*
Mean sp. vol. $C_2H_4Br_2$.*			
97·38	—44	53·38	53·60
	=		
		Sp. vol. ICl.	
		Calculated.	Observed.
Sp. vol. C_2H_4ICl .			
101·03	—44	57·03	56·2
	=		

We have a like instance in the case of propionitrile, C_2H_5CN . The specific volume of this compound is 78·4: subtracting the calculated volume of C_2H_5 , viz., 49·5, we obtain 28·9 as the specific volume of CN, which is identical with the number calculated by Kopp from Faraday's observations.

3. *Determination of the Specific Volumes of Certain Elements.—Chlorine.*—The replacement of an atom of hydrogen by an atom of chlorine in a liquid is accompanied by an increase in the specific volume of about 17·2, hence specific volume of Cl $17 + 5·5 = 22·7$. Thus in the case of trichloroacetyl chloride and acetyl chloride—

Specific volume of CCl_3COCl		=	125·5
" " CH_3COCl		=	74·0
			<hr/>
		3)	51·5
			17·2
Add specific volume of H			5·5
			<hr/>
Specific volume of Cl		=	22·7

So also in the case of ethylene and ethidene chloride and pentachloroethane.

Specific vol. of $CCl_3.CHCl_2..$	=	138·2	CCl_3CHCl_2	=	138·2
„ „ $CH_3CHCl_2..$	=	88·9	$CH_2Cl.CH_2Cl$	=	85·3
		<hr/>			<hr/>
	3)	49·3		3)	52·9
		16·4			17·6
Add specific volume of H.		5·5	Add sp. vol. of H		5·5
		<hr/>			<hr/>
		21·9			23·1

Mean specific volume of Cl..... 22·5

The mean value of Cl calculated from the series—

* Pierre's number included.

is in like manner found to be 22·5. I have included Pierre's results in the calculation.

On the assumption that the specific volume of $\text{CH}_2 = 22$, and that an atom of carbon replaces two atoms of hydrogen without alteration in volume, my observations furnish me with the following estimations of the specific volume of Cl:—

From ethidene chloride.....	22·5
„ acetyl chloride.....	23·3
„ trichloroacetyl chloride	22·7
„ chloral	22·9
„ methene chloride.....	21·6
„ chloroform	22·7
„ chloropicrin	22·5
„ carbon tetrachloride	23·2
Mean.....	22·68

Hence the specific volume of Cl may be taken as 22·7.

Bromine.—The specific volume of bromine appears to be about 28·1. It is found that when an atom of chlorine is replaced by an atom of bromine there is an increase of about 6 in the specific volume.

Specific volume of CHBr_3	103·53
„ „ CHCl_3	84·53
	3) 19·00
	6·3
Add specific volume of Cl	22·7
Specific volume of Br..... =	29·0
From phosphoryl bromochloride and trichloride—	
Specific volume of POBrCl_2	107·38
„ „ POCl_3	101·37
	6·01
Add specific volume of Cl	22·7
Specific volume of Br..... =	28·7
From phosphorus tribromide and trichloride—	
Specific volume of PBr_3	108·31
„ „ PCl_3	93·41
	3) 14·90
	5·0
Add specific volume of Cl	22·7
Specific volume of Br..... =	27·7

The replacement of an atom of hydrogen by one of bromine is accompanied by an increase of 23·9 in the specific volume of the compound. Thus in the case of trichlorobrommethane and chloroform—

Specific volume of CBrCl_3	108·43
" " CHCl_3	84·53
	<hr/>
	23·90
Add specific volume of H	5·5
	<hr/>
Specific volume of Br.	= 29·4

When NO_2 replaces Br in a liquid there is an increase of about 2 in the specific volume of the compound. Thus from trichlorobrommethane and chloropicrin—

Specific volume of $\text{C}(\text{NO}_2)\text{Cl}_3$	110·49
" " CBrCl_3	108·43
	<hr/>
	2·06

And $31·5 - 2·1 = 29·4$ sp. vol. of Br.

Assuming Kopp's values for C and H, my observations furnish the following additional estimations of the specific volume of Br:—

From ethylene bromide	26·7
" bromoform	29·0
" chlorobrommethane	29·0

The mean value deduced from all the observations is 28·1. These numbers it will be observed are in close accordance with those already calculated by Kopp, viz., Cl 22·8 and Br 27·8.

Fluorine.—From arsenic fluoride and arsenic chloride—

Specific volume of AsCl_3	94·37
" " AsF_3	53·84
	<hr/>
	3)40·53
	<hr/>
	13·51

It appears that when an atom of fluorine is replaced by one of chlorine an increase of 13·5 results in the specific volume. Hence the specific volume of F is $22·7 - 13·5 = 9·2$.

Iodine.—The observations with iodine monochloride and ethylene chloriodide furnish the number 36·0 as the specific volume of iodine. This value differs slightly from the value 37·2 (recalculated),* deduced from Kopp and Pierre's observations. The data, however, are insufficient to ascertain the true volume: the expansion of only 6 liquids containing iodine seems to have been determined.

* The atomic weight of iodine was taken by Kopp as 127·1.

By the aid of these values we are able to calculate the specific volume of a number of elementary bodies. We will first take the members of the tetrad group, silicon, titanium, and tin.

Silicon.—From silicon tetrachloride—

	Pierre.	Thorpe.
Specific volume of SiCl_4	121·5	120·8
Less specific volume Cl_4	90·8	90·8
	<hr/> 30·7	<hr/> 30·0

The mean specific volume of Si is 30·3.

Titanium.—From titanium tetrachloride—

	Pierre.	Thorpe.
Specific volume of TiCl_4	124·3	124·5
Less specific volume Cl_4	90·8	90·8
	<hr/> 33·5	<hr/> 33·7

The mean specific volume of Ti is therefore 33·6.

Tin.—From tin tetrachloride—

	Pierre.	Thorpe.
Specific volume of SnCl_4	132·0	131·1
Less specific volume Cl_4	90·8	90·8
	<hr/> 41·2	<hr/> 40·3

The mean specific volume of Sn is 40·8.

These observations show that Kopp's supposition (*Ann. Chem. Pharm.*, **96**, 319), that members of the same family of elements have probably identical specific volumes is not confirmed by experiment. *The specific volume of the element appears to be a function of its atomic weight.*

Evidence of the same fact is afforded by the specific volumes of phosphorus, arsenic, and antimony.

Phosphorus.—From phosphorus trichloride—

	Pierre.	Thorpe.	Buff.
Specific volume of PCl_3 . . .	93·5	93·3	93·3
„ „ Cl_3 . . .	68·1	68·1	68·1
„ „ $\text{P} = \dots$	<hr/> 25·4	<hr/> 25·2	<hr/> 25·2

From phosphorus tribromide—

	Pierre.	Thorpe.
Specific volume of PBr_3 . .	108·4	108·3
„ „ Br_3 . . .	84·3	84·3
„ „ $\text{P} = \dots$	<hr/> 24·1	<hr/> 24·0

From phosphoryl chloride—

	Buff.	Thorpe.
Specific volume of POCl_3 ..	101.4	101.4
Less (7.8 + 68.1) ..	75.9	75.9
Specific volume of P = ..	25.5	25.5
From thiophosphyl chloride—		
Specific volume of PSCl_3		116.1
Less (68.1 + 22.6)		90.7
Specific volume of P =		25.4
From phosphoryl bromochloride—		
Specific volume of POBrCl_2		107.4
Less (45.4 + 28.1 + 7.8)		81.3
Specific volume of P =		26.1
From ethoxyphosphorus chloride—		
Specific volume of $\text{PCl}_2 \cdot \text{C}_2\text{H}_5\text{O}$		128.6
Less (45.4 + 57.3)		92.7
Specific volume of P =		25.9
The mean of the 10 estimations is 25.3.		

Arsenic.—From arsenic trichloride—

	Pierre.	Thorpe.
Specific volume of AsCl_3	94.6	94.4
Less Cl_3	68.1	68.1
	26.5	26.3

From arsenic fluoride—

Specific volume of AsF_3	53.8
Less F_3	27.6
	26.2

The mean of these values is 26.3.

Antimony.—I have recalculated the specific volume of antimony tri-chloride from Kopp's observations on the assumption that the atomic weight of Sb is 120, and that of Cl is 35.37.

According to Kopp, antimony trichloride boils at 223° , under a pressure of 747.7 mm. Reduced boiling point 223.5° . Its expansion by heat may be expressed by the formula—

$$V = 1 + 0.000\ 805\ 4\delta + 0.000\ 010\ 32\delta^2,$$

in which δ = number of degrees above the melting point of the body 73.2 (Kopp). 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 = $\frac{226.11}{2.3377} = 96.72$.

Hence we have for the specific volume of Sb $96.7 - 68.1 = 28.6$.

Vanadium.—The specific volume of this element, as deduced from vanadyl trichloride, depends upon the constitution which is assigned to this compound; and this, in its turn, depends upon the particular atomic value which vanadium is supposed to exert on it. If vanadium be pentad, VOCl_3 must be written—

If triad, then it must be written—

In a former paper (*Proc. Roy. Soc.*, **160**, 1875), I have shown that the specific volumes of phosphoryl trichloride and thiophosphoryl chloride indicate that phosphorus is a triad in these compounds. When oxygen is united to an element by both its affinities, its specific volume is 12.2: when it is attached by only one, its volume is 7.8, a difference of 4.4. Sulphur in like manner has two values, viz., 28.6 and 22.6 — a difference of 6.0.

The specific volume of POCl_3 is	101.3
Subtract $\text{PCl}_3 = (25.3 + 68.1) \dots$	93.4
Specific volume of O	7.9
The specific volume of PSCl_3 is	116.1
Subtract PCl_3	93.4
	22.7

Hence phosphoryl trichloride and thiophosphoryl chloride must be written—

If now vanadyl trichloride be regarded as possessing a similar

constitution to phosphoryl chloride, the specific volume of vanadium is 30·4—

Specific volume VOCl_3	106·3
Less 7·8 + 68·1.....	75·9
	<hr/> 30·4

If, however, it be regarded as pentad it is 26·0—

Specific volume VOCl_3	106·3
Less 12·2 + 68·1	80·3
	<hr/> 26·0

Sulphur.—The specific volumes of thionyl chloride and sulpho-thionyl chloride show that these bodies have an analogous constitution,

viz., $\text{SO} \begin{Bmatrix} \text{Cl} \\ \text{Cl} \end{Bmatrix}$ and $\text{SS} \begin{Bmatrix} \text{Cl} \\ \text{Cl} \end{Bmatrix}$

Specific volume of SSCl_2	90·3
Less Cl_2	45·4
	<hr/> 2)44·9

Specific volume of S	22·5
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Specific volume of SOCl_2	79·1
Less SCl_2	67·9
	<hr/>

Specific volume of O	11·2
----------------------------	------

It would also appear from the specific volume of sulphuryl dichloride that the constitution of this compound must be expressed as—

Specific volume of SO_2Cl_2	86·3
„ „ SOCl_2	79·1
	<hr/>

Specific volume of O	7·2
----------------------------	-----

On the other hand all the oxygen atoms in chlorosulphonic acid have apparently the same specific volume, and hence this body has the constitution—

$$\text{Thus } 22·6 + 3(7·8) + 5·5 + 22·8 = 74·3$$

$$\text{Observed specific volume } \dots = 75·0$$

Buff has determined the specific gravity of sulphuric anhydride at 46—47°, and found it in two concordant experiments to be 1·8103. This gives 44·2 as the specific volume of this substance, a number

which agrees fairly well with that calculated from the specific volume of chlorosulphonic acid, viz., 46·0. This result is confirmatory of the view of the constitution of chlorosulphonic acid, that it is an addition-product of SO_3 and HCl .

The specific volume of disulphuryl chloride appears to indicate that one of the oxygen atoms has the value 12·2, whilst the remaining four have the value 7·8. Thus—

$$(22\cdot5) + 12\cdot2 + 4(7\cdot8) + 2(22\cdot7) = 133\cdot8$$

$$\text{Observed specific volume } \text{S}_2\text{O}_5\text{Cl}_2 = 133\cdot6$$

The specific gravity, boiling point, and rate of thermal expansion of carbon bisulphide have been already observed by Pierre and Buff, and the results lead to the following series of very concordant determinations of specific volume—

Pierre	62·23
Buff.....	62·17
Thorpe	62·11
	<hr/>
Mean	62·19

These numbers indicate that the two sulphur atoms in carbon bisulphide occupy different volumes. Thus—

$$\begin{aligned} &\text{C} + \text{S} + \text{S}'. \\ 11 + 22\cdot6 + 28\cdot6 &= 62\cdot2. \end{aligned}$$

It would be interesting to compare this compound with some of the organic thiocarbonates and with thiocarbonyl chloride, CSCl_2 . A comparison too between ethyl xanthate, $\text{CS} \left\{ \begin{smallmatrix} \text{SC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{smallmatrix} \right.$, and carbonyl disulpho-diethyl, $\text{CO} \left\{ \begin{smallmatrix} \text{SC}_2\text{H}_5 \\ \text{SC}_2\text{H}_5 \end{smallmatrix} \right.$, obtained by the action of sulphuric acid on ethyl sulphocyanate, would doubtless be of value.

Buff (*Jahresb.*, 1868, 652) has determined the specific gravity of ethyl sulphocyanate at its boiling point, 146° : he found 0·8701 and 0·8694, mean 0·8697. This gives the specific volume 100·1, agreeing almost exactly with the calculated number—

$$\begin{aligned} &\text{C}_2\text{H}_5\text{.CN.S.} \\ 22 + 27\cdot5 + 28\cdot9 + 22\cdot6 &= 101\cdot0. \end{aligned}$$

My determination of the specific volume of propionitrile, $\text{C}_2\text{H}_5\text{CN}$, gave 78·4 and $78\cdot4 + 22\cdot6 = 101\cdot0$.

Emmerling and Lengyel found that carbonyl chloride, the analogue of CSCl_2 , boiled at 8° , and had a specific gravity of 1·432 at 0° (*Ann. Chem. Pharm.*, Suppl. 7, 101). The determination is so close to the temperature at which the substance boils that we may take the

specific gravity at that temperature as 1.43 without sensible error. Hence we have for the specific volume $\frac{98.67}{1.43} = 68.9$.

Observed specific volume of COCl_2	68.9
Less specific volume CCl_2	56.6
Volume of O	<u>12.3</u>

Since, as has been shown, the specific volume of oxygen united to an element by both its affinities is 12.2, this would indicate that the constitution of phosgene gas is—

in accordance with the generally received opinion. By analogy, therefore, the sulphur atom in thiocarbonyl chloride and in the thiocarbonates should possess the volume 28.6.

Kopp has already observed that the two atoms of oxygen in sulphur dioxide appear to occupy different volumes. According to Pierre the thermal expansion of sulphur dioxide may be expressed by the formula—

$$V = 1 + 0.001496d + 0.0000223375d^2 - 0.000000495759d^3.$$

$$d = t - 25.85.$$

Its specific gravity at -20.5° was 1.4911, and its boiling point -8° . Hence its specific gravity at the boiling point is 1.455, and its specific volume 43.9.

$$\text{Calculated vol. } 22.6 + 12.2 + 7.8 = 42.6.$$

Andréeff (*Ann. Chem. Pharm.*, **111**; *Ann. Chem. Phys.* [3], **56**, 317), found that sulphur dioxide boils at -10° : its specific gravity at 0° compared with water at the same temperature is 1.4333, and the variation in its specific gravity by temperature may be expressed by the formula—

$$1.4333 - 0.002769t - 0.000000271t^2.$$

From these numbers we obtain the specific volume 43.8.

That the atom of sulphur in the free state occupies the same volume as in combination is shown by Dr. Ramsay's observations. As a mean of several experiments he found the specific gravity of this body at its boiling point (446°) to be 1.4799, which gives the value 21.6 (*loc. cit.*).

Chromium.—The results of the observations on chromyl dichloride, CrO_2Cl_2 , allow of a determination of the specific volume of this element

on the supposition that the compound has a constitution analogous to that of sulphuryl dichloride, SO_2Cl_2 .

Specific volume of CrO_2Cl_2	88.2
" " SO_2Cl_2	86.3
	<hr/>
	1.9
Add specific volume S	22.6
	<hr/>
Specific volume of Cr =	24.5

Dr. Ramsay found that the specific gravity of chromyl dichloride at its boiling point was 1.7538; this gives the specific volume 88.4, which agrees closely with the above result.

If now we arrange the elements in the order of their atomic weights, as in the following table (p. 393), the connection between their specific volumes and these weights becomes apparent.

The main conclusions which I venture to draw from my observations may be briefly stated as follows:—

1. It seems certain that many isomeric liquids, even of the same chemical type, have not identical specific gravities at their respective boiling points, and hence have not identical specific volumes. Such exceptions are more commonly met with in compounds containing carbon and hydrogen: this fact appears to indicate that the specific volume of one or both of these elements is not absolutely invariable. Benzene derivatives especially show a greater departure from the general law than can be fairly attributed to experimental error. Their variations are of the same order as has been shown to occur in the refraction values for these compounds.

2. We must also suppose that of the additional elements, oxygen, sulphur, and nitrogen, have likewise variable specific volumes in conformity with Kopp's conclusions.

3. There is at present no experimental evidence for assuming that any other element has a variable specific volume.

4. Hence in the case of these elements the volume is not modified by the number of the atoms of the particular element in the molecule, and it is therefore altogether independent of the general complexity of the molecule.

5. The different members of a family of elements do not possess identical specific volumes: the volumes of the elements are periodic functions of their atomic weights.

6. The inquiry affords no evidence in support of the hypothesis that the specific volume of an element in combination is modified by any possible variation in the affinity-value which it may possess. The

Atomic Weights.

I.	II.	III.	IV.	V.	VI.
H = 1	C = 11·97	Si = 28·0			Sn = 117·8
	N = 14·01	P = 30·96	Ti = 48	As = 74·9	Sb = 120·0
	O = 15·96	S = 31·98	V = 51·2		
	F = 19·0	Cl = 35·47	Cr = 52·4	Br = 79·75	I = 126·53

Specific Volumes.

I.	II.	III.	IV.	V.	VI.
H = 5·5	C = 11·0	Si = 30·3		—	Sn = 40·8
	N = (?)	P = 25·3	Ti = 33·6	As = 26·3	Sb = 28·6
	O = 7·8 (12·2)	S = 22·6 (28·6)	V = 30·4 (26·0)	—	—
	F = 9·2	Cl = 22·7	Cr = 24·5	Br = 28·1	I = 36·6

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observations on the compounds of phosphorus and sulphur appear to me to be conclusive on this point. It may turn out that the particular value to be assigned to carbon, for example, in the aromatic compounds is slightly different from that which it is found to possess in the fatty acids or the corresponding alcohols and ethers, but there is no question as to the quantivalence of the carbon in these several groups of compounds.

In concluding, I would express my conviction that far too little attention has hitherto been paid to the aid which a knowledge of the specific volume of a body may give towards elucidating its chemical constitution. The chemical history of a substance cannot now be held to be complete until the law of its expansion by heat between the limits at which it is ordinarily a liquid has been ascertained. A simple determination of specific gravity at some indefinite temperature is of no particular value in characterising a body; but the fact may become of great importance if there be added to it the knowledge of the thermal expansion of the substance. We have not to seek far for arguments to support this assertion. The extraordinary multiplication of isomerides which we have witnessed during the last few years demands that the various physical clues to chemical constitution, which are in our possession, should be more closely followed up than they have hitherto been. The mathematical investigations of Professor Cayley have made us familiar with the fact that the number of possible members of one group alone—that of the hydrocarbons of the C_nH_{2n+2} series—almost borders on the infinite; and it seems hopeless to expect that we shall have any other means of identifying, say, the eighteen different bodies of the formula C_8H_{18} , which are theoretically possible, than are afforded to us by differences in their physical characters. Of course the knowledge of the specific volume is only one of the many physical exponents of the constitution of a body that we might have, and it may, of course, happen at times that the information this particular value conveys may not be of great moment, but in the present state of the question, when it is especially important to accumulate facts, the accurate determination of the various data upon which the estimation of this constant depends must ultimately prove of the greatest service.