

XIX.—*The Thermal Expansion and Specific Volumes of certain Paraffins and Paraffin Derivatives.*

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IN the course of an investigation on the viscosity, or internal friction, of liquids, it became necessary to determine the thermal expansion of a number of substances of which the dilatation by heat was hitherto unknown. In the present communication, we desire to put on record the results of these measurements. They have some importance, not only as tending to complete the physical history of the particular liquids, but as furnishing further material towards a fuller discussion of the question of the validity of Kopp's laws of specific volume, and as throwing light on certain aspects of the general problem which have been the subject of experimental inquiry during recent years by Buff, Schiff, Schröder, and more especially by Lossen and his pupils.

All the liquids experimented upon by us had already served for determinations of their internal friction. For some of them we are indebted to the liberality of Dr. Perkin; these are portions of the samples used by him in his investigation on the Magnetic Rotatory Polarisation of Compounds (Trans., 45, 421, 1884). Most of the paraffins were prepared by the late Professor Schorlemmer; the mixed ketones we owe to Professor Japp; the isoprene to Professor Tilden; and the active amyl alcohol to Mr. J. E. Marsh. We beg to express our thanks to these gentlemen for their kindness in placing their preparations at our disposal.

The method of observation employed in the determination of the thermal expansion is identical with that described in the previous communication, the dilatometers used being those of which the numerical constants are therein given.

Pentane, $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$.

The sample, on distillation from sodium wire, boiled between 36° and 38° ; bar. 765.5 mm.

The dilatometrical observations gave:—

<i>t.</i>	Obs.	Calc.	<i>t.</i>	Obs.	Calc.
0°	2148.82	2148.86	19.64	2212.24	2212.22
3.84	2160.90	2160.81	22.15	2220.65	2220.76
7.20	2171.37	2171.42	25.00	2230.69	2230.60
9.80	2179.62	2179.75	27.88	2240.72	2240.68
12.65	2189.04	2188.99	30.49	2249.93	2249.96
16.13	2200.54	2200.46	33.17	2259.62	2259.62

The observed volumes may be expressed by the formula

$$V_t = 2148.864 + 3.0839044t + 0.006555903t^2 + 0.00003437006t^3,$$

which affords the calculated values given above.

Dividing through by the first term and correcting for the expansion of the glass, we obtain

$$V_t = 1 + 0.0214646t + 0.0309319t^2 + 0.016084t^3,$$

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

<i>t.</i>	Vol.	Diff.	<i>t.</i>	Vol.	Diff.
0	1.00000	—	25	1.03880	814
5	1.00740	740	30	1.04716	836
10	1.01497	757	35	1.05574	858
15	1.02272	775	36.3	1.05801	—
20	1.03066	794			

Dr. Perkin found the relative density of pentane to be

$$d_{15^\circ/15^\circ} = 0.63373 \text{ and } d_{25^\circ/25^\circ} = 0.62503.$$

These values, on reduction by means of the foregoing formula, give respectively $d_{0^\circ/4^\circ} = 0.64758$ and 0.64741 ; mean, 0.64750 .

Isopentane (Dimethylethylmethane), $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3$.

The liquid, on distillation from sodium wire, boiled between 29° and 32° ; bar. 763·4 mm. Dr. Perkin, who examined the magnetic rotation of the same sample, found the same boiling point.

The observations for expansion gave:—

<i>t.</i>	Obs.	Calc.	<i>t.</i>	Obs.	Calc.
0°	2146·48	2146·46	16°30	2199·64	2199·74
2·90	2155·64	2155·51	18·38	2207·10	2206·98
5·96	2165·11	2165·26	20·73	2215·27	2215·28
8·36	2173·01	2173·05	22·94	2223·36	2223·20
10·90	2181·41	2181·43	25·18	2231·35	2231·34
13·42	2189·96	2189·90	26·91	2237·54	2237·71

The observed values lead to the following formula for the apparent expansion:—

$$V_t = 2146\cdot462 + 3\cdot0884299t + 0\cdot01084785t^2 + 0\cdot0000146593t^3,$$

which gives the calculated values in the above table.

On dividing through by the first term and correcting for the expansion of the glass, we obtain the following formula, as expressing the absolute expansion of isopentane:—

$$V_t = 1 + 0\cdot0_3146834t + 0\cdot0_5509626t^2 + 0_86979t^3,$$

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

<i>t.</i>	Vol.	Diff.	<i>t.</i>	Vol.	Diff.
0	1·00000	—	20	1·03146	827
5	1·00747	747	25	1·04000	854
10	1·01520	773	30	1·04882	882
15	1·02319	799	30·40	1·04954	—

According to Dr. Perkin (*loc. cit.*), the relative density of isopentane is

$$d_{15^\circ/15^\circ} = 0\cdot62479 \text{ and } d_{25^\circ/25^\circ} = 0\cdot61590.$$

On reduction by means of the foregoing expression, these numbers become respectively

$$d_{0^\circ/4^\circ} = 0\cdot63874 \text{ and } 0\cdot63869. \text{ Mean} = 0\cdot63872.$$

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Isohexane (Dimethylpropylmethane), $(\text{CH}_3)_2\text{CH}\cdot(\text{CH}_2)_2\cdot\text{CH}_3$.

Obtained from Professor Schorlemmer. It boiled at 62° .

The observations for expansion gave :—

t .	Obs.	Calc.	t .	Obs.	Calc.
0°	2140·73	2140·57	29°	2229·53	2229·63
6·15	2158·28	2158·31	34·93	2245·68	2245·73
10·33	2170·36	2170·49	39·68	2261·37	2261·22
15·09	2185·17	2184·53	45·16	2279·78	2279·60
20·68	2200·94	2201·29	49·83	2295·73	2295·72
25·54	2215·85	2216·14	54·66	2312·70	2312·89

The observed values lead to the formula

$$V_t = 2140\cdot569 + 2\cdot8699196t + 0\cdot002005619t^2 + 0\cdot00005791408t^3.$$

Dividing through by the first term and correcting for the expansion of the glass, we obtain for the absolute expansion of isohexane

$$V_t = 1 + 0\cdot02137022t + 0\cdot0697649t^2 + 0\cdot029819t^3,$$

by means of which the following table, showing the relative volume of isohexane at every 10° between 0° and its boiling point, is calculated :—

t .	Vol.	Diff.	t .	Vol.	Diff.
0°	1·00000	—	40°	1·05828	1549
10	1·01383	1383	50	1·07468	1640
20	1·02803	1420	60	1·09217	1749
30	1·04279	1476	62	1·09581	—

Dr. Perkin found the relative density of the same sample

$$d_{15^\circ/15^\circ} = 0\cdot66334 \text{ and } d_{25^\circ/25^\circ} = 0\cdot65538,$$

which, on reduction by means of the foregoing formula, gives

$$d_{0^\circ/4^\circ} = 0\cdot67662 \text{ and } 0\cdot67658. \text{ Mean} = 0\cdot67660.$$

Trimethylethylene (β -Isoamylene), $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CH}_3$.

Prepared from the iodide of dimethylethylcarbinol. On distillation, it boiled between $35\cdot8^\circ$ and $38\cdot0^\circ$; bar. 758·7 mm. A vapour density determination gave 35·19; calculated, 35·00 ($\text{H} = 1$).

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The observations of expansion gave:—

t .	Obs.	Calc.	t .	Obs.	Calc.
0°	2149·77	2149·86	18°31	2208·60	2208·58
3·65	2161·20	2161·18	20·99	2217·60	2217·59
5·77	2167·91	2167·84	24·56	2229·74	2229·79
8·67	2177·12	2177·05	27·69	2240·54	2240·61
11·91	2187·37	2187·49	30·98	2252·23	2252·16
14·76	2196·86	2196·81	38·69	2261·81	2261·81

From the observed values the following formula results:—

$$V_t = 2149.866 + 3.072632t + 0.007185091t^2 + 0.00000708768t^3.$$

This, by dividing through by the first term and correcting for the expansion of the glass, yields as the formula for the absolute expansion of the trimethylethylene

$$V_t = 1 + 0.02145871t + 0.0338435t^2 + 0.0339536t^3.$$

From this is calculated the following table, giving the relative volume of the liquid for every 5° between 0° and its boiling point:—

t .	Vol.	Diff.	t .	Vol.	Diff.
0	1.00000	—	25	1.03864	809
5	1.00738	738	30	1.04690	826
10	1.01493	755	35	1.05535	845
15	1.02265	772	36·4	1.05774	—
20	1.03055	790			

The relative density of trimethylethylene was found by Dr. Perkin to be

$$d_{15^\circ/15^\circ} = 0.67037. \quad d_{25^\circ/25^\circ} = 0.66143,$$

which, by calculation with the above volumes, gives

$$d_{0^\circ/4^\circ} = 0.68498 \text{ and } 0.68501. \quad \text{Mean} = 0.68499.$$

Isoprene (Pentine), C₅H₈.

Obtained by Dr. Tilden from turpentine. On distillation, the greater part boiled between 35.5° and 36.1°. A vapour density determination gave 35.73; calculated, 34.0.

The observations of thermal expansion gave:—

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<i>t.</i>	Obs.	Calc.	<i>t.</i>	Obs.	Calc.
0°	2129·71	2229·64	17°89	2185·48	2185·48
4·56	2143·60	2143·58	20·93	2195·40	2195·40
6·41	2149·21	2149·28	23·85	2205·12	2205·17
9·09	2157·40	2157·59	26·98	2215·79	2215·67
12·45	2168·20	2168·12	29·56	2224·73	2224·56
15·05	2176·50	2176·36	32·60	2235·03	2235·26

The observed values lead to the formula

$$V_t = 2129.636 + 3.0470972t + 0.002035399t^2 + 0.0001192315t^3,$$

from which the calculated numbers are derived. After dividing by the first term and correcting for the expansion of the glass, the formula for the true expansion is obtained

$$V_t = 1 + 0.0214603t + 0.0699793t^2 + 0.0560149t^3.$$

From this the following table of the relative volumes of isoprene is calculated :—

<i>t.</i>	Vol.	Diff.	<i>t.</i>	Vol.	Diff.
0	1.00000	—	25°	1.03801	796
5	1.00733	733	30	1.04622	821
10	1.01476	743	35	1.05473	851
15	1.02232	756	35·8	1.05613	—
20	1.03005	773			

The relative density as determined by Dr. Perkin was

$$d_{12^\circ/12^\circ} = 0.6794.$$

On reduction by the above formula, this yields

$$d_{0^\circ/4^\circ} = 0.6912.$$

Trimethyl Carbinol, (CH₃)₃COH.

The sample of this substance, received from Dr. Perkin, had been distilled with baryta and kept in a fused state over anhydrous copper sulphate for many weeks. On distillation, it boiled between 81.9° and 82.4°; bar. 756.1 mm.

The determinations of vapour density would seem to indicate that

the sample, in spite of the prolonged desiccation, was still imperfectly dehydrated.

Found 34·62 and 34·97

Calculated 37·00

Unfortunately the quantity of the substance was insufficient to enable us to submit to further dehydration.

The dilatometrical observations gave :—

<i>t.</i>	Obs.	Calc.	<i>t.</i>	Obs.	Calc.
19°59	2134·04	2133·57	51°96	2225·54	2225·58
24·19	2145·88	2145·97	57·10	2241·68	2241·78
31·25	2164·92	2065·30	62·12	2258·01	2257·97
35·96	2178·48	2178·48	67·15	2274·97	2274·90
41·13	2193·24	2193·26	72·50	2293·71	2293·66
46·21	2208·19	2208·17	77·06	2310·17	2310·29

These observed values yield

$$V_t = 2081·418 + 2·6706988t - 0·0019138328t^2 + 0·0000752391t^3.$$

by which the calculated numbers in the above table are obtained.

From this the following formula for the absolute expansion of the trimethylcarbinol is obtained :—

$$V_t = 1 + 0·002131261t - 0·088155t^2 + 0·03612087t^3,$$

by which the following table, giving the relative volumes of the liquid for each 10° between 0° and its boiling point, is calculated on the assumption that the expansion formula is applicable down to 0° :—

<i>t.</i>	Vol.	Diff.	<i>t.</i>	Vol.	Diff.
0°	1·00000	—	50°	1·06794	1453
10	1·01307	1307	60	1·08338	1544
20	1·02619	1312	70	1·09995	1657
30	1·03956	1337	80	1·11786	1791
40	1·05341	1385	82·2	1·12201	—

The relative density as determined by Dr. Perkin is

$$d_{25^\circ/25^\circ} = 0·78356. \quad d_{35^\circ/35^\circ} = 0·77605.$$

On reduction by means of the foregoing formula, we obtain for the density at 0°

$$d_{0^\circ/4^\circ} = 0·80695 \text{ and } 0·80737. \quad \text{Mean} = 0·80716.$$

Dimethylethylcarbinol, $\text{CH}_3\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_3$.

Received from Dr. Perkin. After standing over anhydrous copper sulphate for five months, the liquid was found to boil between $101\cdot6^\circ$ and $102\cdot5^\circ$; bar. 766·9 mm.

Two determinations of its vapour density gave 41·00 and 41·37; calculated, 44·0.

In spite of the prolonged digestion with copper sulphate, the liquid was apparently not completely dehydrated.

The expansion observation gave the following results:—

<i>t.</i>	Obs.	Calc.	<i>t.</i>	Obs.	Calc.
0°	2126·85	2126·66	54°34	2262·35	2262·14
10°62	2150·43	2150·52	62°57	2286·74	2286·36
17°70	2166·90	2167·00	71°35	2312·99	2313·58
27°45	2190·35	2190·57	79°22	2339·28	2339·31
36°19	2213·28	2213·20	90°36	2377·62	2378·03
45°02	2236·25	2236·11	96°64	2401·58	2401·14

From the observed numbers the following formula is derived:—

$$V_t = 2126\cdot659 + 2\cdot2044768t + 0\cdot003687091t^2 + 0\cdot000029917423t^3,$$

by means of which the calculated values are obtained.

Dividing by the first term and correcting for the expansion of the glass, we obtain the formula for the absolute expansion

$$V_t = 1 + 0\cdot02106608 + 0\cdot05176432t^2 + 0\cdot0141189t^3.$$

From this is calculated the table of volumes of the liquid at every 10° between 0° and its boiling point:—

<i>t.</i>	Vol.	Diff.	<i>t.</i>	Vol.	Diff.
0	1·00000	—	60	1·07337	1389
10	1·01085	1085	70	1·08811	1474
20	1·02214	1129	80	1·10381	1570
30	1·03395	1181	90	1·12053	1672
40	1·04637	1242	100	1·13837	1784
50	1·05948	1311	101·3	1·14077	—

Dr. Perkin found the relative density of the liquid to be

$$d_{15/15} = 0\cdot81438,$$

$$d_{25/25} = 0\cdot80689,$$

which, after reduction by means of formula given above, gives

$$d_{0^\circ/0^\circ} = 0\cdot82707 \text{ and } 0\cdot82677. \text{ Mean } 0\cdot8269,$$

which is almost identical with the number found by Wischnegradsky (*Ann. Chim. Phys.*, **190**, 334), viz., 0·8270.

Optically Inactive Amyl Alcohol, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$.

Prepared for us by Mr. A. Greeves, Assoc. Royal College of Science, by Pasteur's method. When examined in the Soleil-Duboscq polarimeter with a sodium flame, not the least indication of rotation was apparent. After dehydration by anhydrous copper sulphate, it boiled constantly between 131·75° and 131·80°; bar: 762·0 mm.; corr. and red. b. p. = 131·4°.

A determination of its vapour density gave 44·18; calculated, 44·0 (H = 1).

The observations with the dilatometer gave:—

<i>t</i> .	Obs.	Calc.	<i>t</i> .	Obs.	Calc.
0°	2129·07	2128·63	72°48	2280·42	2280·24
13·05	2153·47	2153·63	83·28	2307·24	2307·30
24·88	2176·48	2176·76	97·13	2344·54	2344·66
36·13	2199·21	2199·44	107·87	2376·20	2375·89
48·24	2224·96	2224·89	116·99	2404·49	2404·28
59·59	2250·14	2249·97	125·96	2433·35	2433·86

The observed values lead to the following formula:—

$$V_t = 2128\cdot63 + 1\cdot9042945t + 0\cdot0005064091t^2 + 0\cdot0000286915t^3,$$

from which the calculated values are obtained.

This leads to the formula

$$V_t = 1 + 0\cdot0392410t + 0\cdot0626428t^2 + 0\cdot01348589t^3,$$

by which is calculated the volumes of the liquid for every 10° between zero and the boiling point as given in the following table:—

<i>t</i> .	Vol.	Diff.	<i>t</i> .	Vol.	Diff.
0	1·00000	—	80	1·08252	1191
10	1·00928	928	90	1·09514	1262
20	1·01870	942	100	1·10854	1340
30	1·02832	962	110	1·12280	1426
40	1·03825	993	120	1·13800	1520
50	1·04855	1030	130	1·15423	1623
60	1·05931	1076	131·4	1·15659	—
70	1·07061	1130			

Two separate observations of the density were made with the results

$$d_{0^{\circ}/4^{\circ}} = 0.82535 \text{ and } 0.82536.$$

Optically Active Amyl Alcohol, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\text{OH}$.

We are indebted to Mr. J. E. Marsh, Oxford, for the specimen of optically active amyl alcohol which has served for our observations. Its rotatory power was $-7^{\circ} 34'$ per 200 mm. at 10° . It was placed over fused potassium carbonate for 18 days and then distilled. It boiled between 127.5° and 129.5° ; bar. 751.8 mm.

A determination of its vapour density gave 43.46; calculated, 44.00 ($H = 1$).

The observations for expansion gave:—

t .	Obs.	Calc.	t .	Obs.	Calc.
0.0	2126.82	2126.85	71.34	2277.28	2277.30
12.47	2150.04	2150.09	80.76	2301.58	2301.57
24.55	2173.64	2173.55	92.65	2334.13	2334.03
35.23	2195.32	2195.24	100.04	2355.08	2355.38
47.17	2220.82	2220.76	109.89	2385.19	2385.36
58.28	2245.76	2245.89	121.35	2423.04	2422.56

These observations lead to the following formula for the apparent expansion:—

$$V_t = 2126.85 + 1.8306664t + 0.00237863t^2 = 0.0000215606t^3,$$

by means of which the calculated values in preceding table are derived.

Dividing by the first term and correcting for the expansion of the glass, we obtain the formula for the true expansion of optically active amyl alcohol

$$V_t = 1 + 0.089023t = 0.08114376t^2 + 0.081017029t^3,$$

by means of which we obtain the following table of the volume at every 10° up to the boiling point:—

t .	Vol.	Diff.	t .	Vol.	Diff.
0	1.00000	—	70	1.07141	1168
10	1.0903	903	80	1.08375	1234
20	1.01834	931	90	1.09680	1305
30	1.02801	967	100	1.11063	1383
40	1.03809	1008	110	1.12530	1467
50	1.04864	1055	120	1.14087	1557
60	1.05973	1109	128.7	1.15520	

Two observations of the density gave

$$d\ 0^{\circ}/4^{\circ} = (1) 83293, \text{ and } (2) 0.83311. \text{ Mean } 0.83302.$$

Methyl Ethyl Ketone, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$.

Prepared from ethylic methacetoacetate by Böcking's method (*Annalen*, **204**, 17). After treatment with anhydrous copper sulphate, it boiled between 79° and 83° ; bar. 772.8 mm. The quantity of the liquid was insufficient to allow of fractionation.

A determination of vapour density gave 35.14; calculated, 36.00.

The observations for expansion gave:—

<i>t.</i>	Obs.	Calc.	<i>t.</i>	Obs.	Calc.
0.0	2129.70	2129.96	41.70	2244.53	2244.25
7.40	2148.69	2148.58	48.87	2265.95	2266.02
14.28	2166.73	2166.57	55.67	2286.98	2287.18
20.93	2184.68	2184.55	62.45	2308.79	2308.77
28.75	2206.69	2206.42	69.10	2330.41	2330.37
34.96	2223.91	2224.32	75.61	2351.86	2351.91

The observed volumes lead to the apparent expansion formula

$$V_t = 2129.963 + 2.464481t + 0.007106213t^2 - 0.00001157599t^3,$$

from which the calculated numbers are obtained. On dividing by the first term, and correcting for the expansion of the glass, the formula for the absolute expansion is obtained

$$V_t = 1 + 0.02118654t + 0.0337043t^2 - 0.0533645t^3,$$

from which is calculated the following table of relative volumes:—

<i>t.</i>	Vol.	Diff.	<i>t.</i>	Vol.	Diff.
0	1.00000	—	50	1.06709	1458
10	1.01220	1220	60	1.08217	1508
20	1.02504	1284	70	1.09774	1557
30	1.03849	1345	80	1.11376	1602
40	1.05251	1402	80.6	1.11474	—

Two determinations of the density were made, giving results

$$(1) d\ 0^{\circ}/4^{\circ} = 0.82964, (2) d\ 0^{\circ}/4^{\circ} = 0.82958. \text{ Mean } 0.82961.$$

Methyl Propyl Ketone, $\text{CH}_3(\text{CH}_2)_2\text{CO}\cdot\text{CH}_3$.

A sample of this liquid, lent to us by Dr. Japp, was placed over anhydrous copper sulphate and submitted to fractional distillation. The portion used for the observations boiled between $102\cdot45^\circ$ and $102\cdot80^\circ$; bar. 775·4 mm.

Two determinations of vapour density gave 42·97 and 42·78; calculated, 43·00.

The observations for thermal expansion gave:—

<i>t</i> .	Obs.	Calc.	<i>t</i> .	Obs.	Calc.
0°	2132·09	2132·12	53°	2271·30	2271·37
8·72	2152·94	2152·94	62·93	2298·06	2298·06
18·09	2176·10	2176·07	71·70	2324·23	2324·16
27·06	2198·94	2198·97	80·73	2351·40	2351·82
35·77	2220·02	2221·92	83·72	2361·51	2361·15
44·66	2246·00	2246·07	89·74	2380·28	2380·22

The calculated values are obtained by means of the formula

$$V_t = 2132\cdot120 + 2\cdot348284 + 0\cdot00446257t^2 + 0\cdot000001971608t^3,$$

derived from the observed numbers.

From this we obtain the formula for the true expansion

$$V_t = 1 + 0\cdot0_2113087t + 0\cdot0_2212550t^2 + 0\cdot0_398644t^3,$$

by means of which the following table of relative volumes is calculated:—

<i>t</i> .	Vol.	Diff.	<i>t</i> .	Vol.	Diff.
0	1·00000	—	60	1·07572	1374
10	1·01152	1152	70	1·08991	1419
20	1·02347	1195	80	1·10458	1467
30	1·03587	1240	90	1·11971	1513
40	1·04870	1283	100	1·13533	1562
50	1·06198	1328	101·7	1·13803	—

Dr. Perkin found the relative density of methyl propyl ketone to be

$$d_{15^\circ/15^\circ} = 0\cdot81238 \text{ and } 0\cdot81233. \quad \text{Mean } 0\cdot81236.$$

$$d_{25^\circ/25^\circ} = 0\cdot80447 \text{ and } 0\cdot80423. \quad \text{Mean } 0\cdot80435.$$

These, by reduction by means of above formula, give

$$d\,0^{\circ}/4^{\circ} = (1) \, 0.82593 \text{ and } 0.82578. \text{ Mean } 0.82585.$$

Diethyl Ketone, $\text{CH}_3\text{CH}_2\text{CO}\cdot\text{CH}_2\text{CH}_3$.

Prepared from barium propionate by Krafft's method.

It boiled between 101.2° and 102.0° ; bar. 745.3 mm.

A vapour density determination gave 41.98; calculated, 43.0.

The observations for expansion were as follows:—

<i>t.</i>	Obs.	Calc.	<i>t.</i>	Obs.	Calc.
0°	2130.02	2129.91	53°31'	2269.75	2269.74
12.03	2159.22	2159.29	62.20	2295.73	2295.67
20.74	2181.27	2181.31	70.19	2319.61	2319.67
29.57	2204.32	2204.32	78.66	2345.77	2345.86
36.66	2223.24	2223.30	88.04	2375.76	2375.79
45.91	2248.82	2248.77	95.06	2398.98	2398.85

These observations lead to the formula for the apparent expansion

$$V_t = 2129.908 + 2.3938717t + 0.003942079t^2 + 0.0000067039556t^3,$$

from which are derived the calculated values in the foregoing table. After dividing by the first term and correcting for the expansion of the glass, the following formula is obtained for the true expansion:—

$$V_t = 1 + 0.02115342t + 0.05188396t^2 + 0.05320211t^3,$$

by means of which the following table of relative volumes of diethyl ketone is calculated:—

<i>t.</i>	Vol.	Diff.	<i>t.</i>	Vol.	Diff.
0	1.00000	—	60	1.07668	1390
10	1.01173	1173	70	1.09167	1439
20	1.02385	1212	80	1.10597	1490
30	1.03638	1253	90	1.12140	1543
40	1.04936	1298	100	1.13738	1598
50	1.06278	1342	102.1	1.14081	—

The density at 0° is given by Chancel (*Compt. rend.*, **99**, 1055) = 0.8335.

Propionic Anhydride, (CH₃CH₂CO₂)O.

A quantity of this liquid, prepared by Kahlbaum, was shaken with a small quantity of phosphoric oxide for a few minutes, decanted, and submitted to fractional distillation. The portion employed for the observations boiled constantly between 168·55° and 169·50°; bar. 765·1 mm.

Observations for expansion gave:—

<i>t.</i>	Obs.	Calc.	<i>t.</i>	Obs.	Calc.
0·0	2124·85	2124·32	89·01	2341·04	2340·72
16·59	2161·62	2162·00	104·77	2384·46	2384·69
30·22	2193·40	2193·55	114·72	2413·64	2413·73
44·71	2227·89	2227·88	127·24	2452·03	2451·82
59·72	2264·58	2264·61	134·64	2475·28	2475·22
75·09	2303·75	2303·73	146·82	2515·01	2515·25

The observations yield the formula

$$V_t = 2124\cdot324 + 2\cdot255179t + 0\cdot00074701t^2 + 0\cdot00001381712t^3$$

for the apparent expansion, and from this the calculated values in above table are obtained.

After necessary correction, this leads to the following formula for the true expansion:—

$$V_t = 1 + 0\cdot0_2109109t + 0\cdot0_638295t^2 + 0\cdot0_6651461t^3,$$

from which the table of volumes is calculated:—

<i>t.</i>	Vol.	Diff.	<i>t.</i>	Vol.	Diff.
0	1·00000	—	90	1·10605	1298
10	1·01095	1096	100	1·11945	1340
20	1·02203	1107	110	1·13332	1387
30	1·03325	1128	120	1·14770	1438
40	1·04467	1142	130	1·16263	1493
50	1·05633	1166	140	1·17813	1550
60	1·06825	1192	150	1·19427	1614
70	1·08049	1224	160	1·21106	1679
80	1·09307	1258	168·6	1·22607	

The relative density is given by Dr. Perkin (*J. Chem. Soc.*, 1857, 11) as = 1·0169 at 15°, which, on reduction by the above formula, gives $d\ 0^\circ/4^\circ = 1\cdot0336$.

Methyl Sulphide, (CH₃)₂S.

A large quantity of this liquid, belonging to the chemical collections of the Royal College of Science, was dried over phosphoric oxide and fractionated. The greater portion boiled constantly between 37·2° and 37·52°; bar. 756·4 mm.; corrected b. p. = 37·5°.

A determination of vapour density gave 31·17. Calculated 31·00.

Two separate series of observations on the expansion were performed with the following results:—

<i>t.</i>	Obs.	Calc.	<i>t.</i>	Obs.	Calc.
0°	2141·59	2141·49	0°	2143·89	2143·77
4·61	2154·27	2154·32	2·96	2152·02	2152·02
8·89	2166·49	2166·44	6·56	2162·25	2162·30
12·11	2175·52	2175·69	9·08	2169·56	2169·54
15·18	2184·78	2184·65	12·09	2178·20	2178·28
18·19	2193·70	2193·55	15·80	2189·27	2189·22
20·70	2201·19	2201·08	18·56	2197·44	2197·45
23·91	2210·91	2210·86	20·91	2204·53	2204·55
26·84	2219·87	2219·93	24·11	2214·39	2214·36
29·65	2228·92	2228·78	29·47	2231·33	2231·13
32·55	2238·01	2238·06	33·39	2243·68	2243·70
35·03	2246·14	2246·13	35·34	2249·88	2250·06

The observed values lead to the apparent expansion formula

$$\text{I. } V_t = 2141·49 + 2·762640t + 0·0044723659t^2 + 0·00005527925t^3,$$

$$\text{II. } V_t = 2143·773 + 2·7935835t + 0·004487438t^2 + 0·0000442832t^3,$$

from which the above series of calculated numbers are respectively obtained.

From the mean of these formulæ, by dividing by the first term and correcting for the expansion of the glass, the true expansion formula is obtained

$$V_t = 1 + 0·0132607t + 0·021302146t^2 + 0·0232968t^3,$$

which yield the following table of volumes:—

<i>t.</i>	Vol.	Diff.	<i>t.</i>	Vol.	Diff.
0°	1·00000	—	25°	1·03485	729
5	1·00660	669	30	1·04233	748
10	1·01350	681	35	1·05002	769
15	1·02045	695	37·5	1·05395	—
20	1·02756	711			

Two determinations of density were made :—

$$\left. \begin{array}{l} (1.) d_{0^{\circ}/4^{\circ}} = 0.87026 \\ (2.) d_{0^{\circ}/4^{\circ}} = 0.87019 \end{array} \right\} \text{Mean } 0.87022.$$

Isobutylene Bromide, $(\text{CH}_3)_2\text{CBr}\cdot\text{CH}_2\text{Br}$.

A quantity of this substance, procured from Kahlbaum, was placed over phosphoric oxide for some days and then distilled. It boiled completely between 149.1° and 149.85° ; bar. 752.5 mm.; corrected b. p. 149.6° .

The observations for expansion gave :—

<i>t.</i>	Obs.	Calc.	<i>t.</i>	Obs.	Calc.
0°	2129.27	2128.81	$77^{\circ}.76$	2291.04	2290.87
$14^{\circ}.64$	2157.60	2157.84	$88^{\circ}.47$	2315.56	2315.45
$26^{\circ}.30$	2181.06	2181.29	$106^{\circ}.11$	2357.40	2357.69
$38^{\circ}.82$	2206.88	2206.90	$117^{\circ}.11$	2384.95	2385.28
$51^{\circ}.65$	2233.77	2133.76	$129^{\circ}.49$	2417.79	2417.59
$65^{\circ}.28$	2263.12	2263.11	$134^{\circ}.60$	2431.46	2431.34

the calculated values being obtained from the formula

$$V_t = 2128.811 + 1.971646t + 0.00061783t^2 + 0.00001064332t^3.$$

This leads to the following formula for the true expansion of the liquid :—

$$V_t = 1 + 0.0395566t + 0.031753t^2 + 0.0500821t^3,$$

from which the following table of the relative volume of isobutylene bromide at every 10° between 0° and the boiling point is calculated :—

<i>t.</i>	Vol.	Diff.	<i>t.</i>	Vol.	Diff.
0°	1.00000	—	80°	1.08105	1088
10	1.00959	959	90	1.09223	1118
20	1.01928	969	100	1.10375	1152
30	1.02909	981	110	1.11563	1188
40	1.03905	996	120	1.12791	1228
50	1.04920	1015	130	1.14060	1269
60	1.05956	1036	140	1.15378	1316
70	1.07017	1061	$159^{\circ}.61$	1.16685	—

The relative density was found by Dr. Perkin to be

$$d_{15^{\circ}/15^{\circ}} = 1.74343. \quad d_{25^{\circ}/25^{\circ}} = 1.73083.$$

These, on reduction by aid of above formula give—

$$d\,0^{\circ}/4^{\circ} = 1.76745 \text{ and } 1.76756. \text{ Mean } 1.7675.$$

Although the main object of the observations here recorded was, as already stated, to furnish data for the reduction of measurements of the viscosity of the particular liquids, for which purpose it may be remarked, the thermal expansion requires to be known with only approximate accuracy, the determinations are of service as affording information on the question of the specific volumes of the special substances, more particularly in relation to the deductions of Lossen (*Annalen*, 214, 81; 225, 109; 233, 316; 254, 42).

According to Lossen the specific volumes of the greater number of compounds containing carbon, hydrogen, and oxygen, which have hitherto been determined, may be calculated by the formula

$$\text{Sp. vol., } C_nH_mO_p(\mu) = (10.24 \pm x0.5)(n + p) + (5.12 \pm x0.25)m \pm \frac{1}{4}(n - 2)^2 \pm 1.4\mu.$$

In this equation x denotes a number between 0 and 1, which varies with different homologous series, but which is constant for the members of one and the same series. The sign μ represents the number of hydrogen atoms required to convert the formula into that of a saturated compound. The term $\frac{1}{4}(n - 2)^2$ is introduced to compensate for the increase in the value corresponding to CH_2 , as the molecular weight increases. Gartenmeister (*Annalen*, 233, 304) having shown that in the case of the fatty esters the mean increase is 0.5, Lossen adds the term $\left(\frac{1}{2} + \frac{2}{2} + \frac{3}{2} + \dots \frac{n-3}{2}\right)$, which he erroneously states is equal to $\frac{1}{4}(n - 2)^2$, a number always subsequently employed, but which, as comparison of his numbers shows, serves to give good agreement with observed values.

For the majority of aliphatic compounds the formula

$$C_nH_mO_p = 10.45(n + p) + 5.225m + \frac{1}{4}(n - 2)^2 + 1.5\mu$$

gives the results in good agreement with the observed values. For the alcohols, however, the expression becomes

$$C_nH_mO_p = 10.1(n + p) + 5.05m + \frac{1}{4}(n - 2)^2 + 1.35\mu.$$

If it be assumed, as seems highly probable, that for all the members of a series of similarly constituted compounds the same influences are existent, causing the specific volumes to exhibit variations from the additive quantities which Kopp's values assume them to be, then we may regard the variable x as a term which takes account, and may be regarded as the measure of these disturbing influences, and which,

though constant for the members of the same series, should, as before stated, vary for other homologous series of compounds.

It may be desirable to summarise here the quantitative values upon which the calculations of the specific volumes of the particular liquids is based. The following table gives the boiling point under a standard atmosphere, together with the density at 0° and at the boiling point, the observed specific volume, together with that calculated by means of Kopp's values, and that calculated by the formula of Lossen. The atomic weights taken for the calculation of the specific volumes are O = 16, C = 12, and, in the reduction of the relative densities, the density of water has been taken from Rossetti's tables.

	B. p.	Density at 0°.	Density at b. p.	Specific volume.		
				Obs.	Kopp.	Lossen.
	° C.					
Pentane	36·3	0·64750	0·61200	117·6	121·0	117·2
Isopentane	30·4	0·63872	0·60857	118·3	121·0	117·2
Isohexane.....	62·0	0·67660	0·61744	139·3	143·0	139·8
Amylene.....	36·4	0·68499	0·64759	108·1	110·0	109·7
Isoprene	35·8	0·69120	0·65450	103·9	99·0	102·3
Trimethyl carbinol	82·2	0·80716	0·71940	102·8	106·8	102·0
Dimethyl ethyl carbinol...	101·3	0·82690	0·72480	121·4	128·8	123·4
Inactive amyl alcohol	131·4	0·82536	0·71362	123·3	128·8	123·4
Active amyl alcohol	128·7	0·83302	0·72111	122·0	128·8	123·4
Methyl ethyl ketone.....	80·6	0·82961	0·74422	96·7	100·2	95·1
Methyl propyl ketone.....	101·7	0·82585	0·72568	118·5	122·2	117·2
Diethyl ketone.....	102·1	0·83350	0·73060	117·7	122·2	117·2
Propionic anhydride.....	168·6	1·03360	0·84310	154·2	153·2	150·3
Methyl sulphide.....	37·5	0·87022	0·82567	75·1	77·6	75·8
Isobutylene bromide.....	149·6	1·76750	1·51470	142·6	144·2	142·8

It will be seen that, with the exception of that for propionic anhydride, all the observed numbers differed considerably from those calculated by means of Kopp's values. On the other hand, they show, in the main, a fairly satisfactory agreement with the values calculated by Lossen's formula. It is noteworthy that the observed value for acetic anhydride deduced from Kopp's experiments, viz., 109·9, is also greatly in excess of the value calculated by Lossen's formula. If, however, we take Lossen's slightly higher values, *e.g.*, $\text{CO}_2\text{H} = 10·74$, as given for the oxalic ethers we obtain values for

these oxides which are in better agreement with the results of observation, thus :—

	Observed.	Calculated.
Acetic anhydride.....	109·9	108·4
Propionic anhydride...	154·2	154·4

ADDENDUM.—As the relation of our results to Schröder's theory of specific volume was raised in the course of the discussion on this paper, we append here the values of the steres calculated by means of Schröder's rules :—

	No. of steres.	Value of stere.		No. of steres.	Value of stere.
Pentane.....	17	6·92	Methyl ethyl ketone..	14	6·91
Isopentane.....	17	6·96	Methyl propyl ketone	17	6·97
Isohexane.....	20	6·96	Diethyl ketone.....	17	6·92
Trimethylethylene ...	16	6·76			
Isoprene.....	15	6·93	Isobutylene bromide..	20	7·13
Trimethyl carbinol ...	15	6·85	Propionic anhydride.	21	7·34
Dimethyl ethyl carb- inol	18	6·74	or....	22	7·01
Inactive amyl alcohol.	18	6·85			
Active amyl alcohol ..	18	6·78			

The variations in the value of the stere are of the same order as in similar compounds calculated by Schröder. Thus—

	Variation of stere.	Schröder.
Hydrocarbons....	6·76 to 6·96	6·87 to 7·09
Alcohols	6·74 „ 6·85	6·72
Ketones.....	6·91 „ 6·97	—

The common value 6·90 leads to results which are in fair accord with the observed numbers:

Stere = 6·90.

	Calc.	Obs.		Calc.	Obs.
Pentane	117·3	117·6	Methyl ethyl ketone ..	96·6	96·7
Isopentane.....	117·3	118·3	Methyl propyl ketone .	117·3	118·5
Isohexane.....	138·0	139·3	Diethyl ketone	117·3	117·7
Amylene.....	110·4	108·1	Isobutylene bromide..	138·0	142·6
Isoprene.....	103·5	103·9			
			Methyl sulphide.....	75·9	75·1
Trimethyl carbinol ...	103·5	102·8			
Dimethyl ethyl carbinol	124·2	121·4	Propionic anhydride ..	151·8	154·2
Inactive amyl alcohol..	124·2	123·3			
Active amyl alcohol....	124·2	122·0			

It will be seen that the agreement between the observed and calculated values is better than that given by Kopp's rules, and is quite as good as that obtained by the use of Lossen's formulæ.
