

IX.—*On the Specific Volume of Chloral.*

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AMONG the substances selected by Dr. Thorpe as constituting the experimental groundwork of his investigation "On the Relation between the Molecular Weights of Substances and their Specific

Gravities when in the Liquid State" (*Chem. Soc. J.*, March, *et seq.*, 1880) was chloral. The main point of interest connected with the determination of the specific volume of this body arises from its relation to aldehyde, and from the fact, therefore, that its oxygen-atom would presumably have the same value as in that compound. It was part of Dr. Thorpe's original scheme of work to determine how far the introduction of the three chlorine-atoms in place of hydrogen would modify the specific volume of the compound. Considerable difficulty was met with in procuring this body in a fit state for physical examination, owing to the persistency with which gas-bubbles made their appearance in the liquid when it was heated much beyond 60°. No two samples of chloral could be obtained of identical specific gravity, even although prepared and dehydrated under similar conditions. This circumstance is undoubtedly connected with the tendency of chloral to pass into a polymeric modification, but unfortunately the causes determining this tendency are too incompletely understood to be applied in maintaining this body in a stable condition.

At Dr. Thorpe's suggestion I have again essayed to determine the specific volume of chloral. The greatest care was taken to dehydrate the liquid, and to avoid the formation of free hydrochloric acid, which appears to have a marked influence in polymerising the substance. Although a considerable interval of time has elapsed since the observations which form the subject of the present communication were made, the chloral used has maintained its limpidity unimpaired, and there is no evidence of the formation of metachloral within it.

The liquid was prepared from commercial recrystallised hydrate by treating it with strong oil of vitriol, and afterwards distilling it twice over lime. It was observed that on adding the chloral hydrate to strong sulphuric acid the temperature was reduced by 17°; the temperature of the acid having been 13°, and that of the mixture falling to -4°. The dehydrated chloral was always redistilled before each operation.

In order to verify its purity its vapour-density was determined with the following results. The apparatus employed was the modified Gay-Lussac-Hofmann apparatus described by Dr. Thorpe:—

Weight of liquid	0.1898 gram.
Volume of vapour, corrected for expansion of glass, error of meniscus, &c.	91.74 c.c.
Temperature	99.96°
Barometer (reduced)	758.93 mm.
Mercury column (reduced).....	426.9 „
Found 72.21	Calculated 73.48

Determination of Boiling Point.—This was effected in the manner

described in the memoir above referred to, and with the same thermometers.

The liquid began to boil at 96° , and that portion was collected separately which came over between 96.8° and 97.3° (uncorr.).

Observed temperature	97.05°
Temperature of the cooled column	23.8°
Length of the cooled column in degrees ..	42
Barometer (reduced)	747.7 mm.
Corrected and reduced boiling point 97.73° .	

Specific Gravity.—The specific gravity was determined upon two samples in separate bottles. The bottles used had graduated stems, and were fitted with ground-glass stoppers. The weighings were made by the method of vibrations, and the weights are reduced to a vacuum. The specific gravities are finally reduced to the temperature of 0° , and compared with water at 4° by means of the tables of expansion given below:—

Bottle 1.

Weight of chloral at div. 40 and 15.4°	8.99126 grams.
Weight of water at div. 40 and at 15.04° ..	5.92866 „
Vol. of water at 15.4°	1.000904
Vol. of water at 15.04	1.000847
Sp. gr. at 15.4° compared with water of same temp.	1.5167
Vol. of chloral at 15.4°	1.017424
Vol. of water at 15.4	1.000904

Bottle 2.

Weight of chloral at div. 35.5 and 15.4° ..	7.83577 grams.
Weight of water at div. 35.5 and 15.4	5.16691 „
Vol. of water at 15.4°	1.000904
Vol. of water at 15.04	1.000847
Sp. gr. at 15.4° compared with water of same temp.	1.5166
Vol. of chloral at 15.4°	1.017424
Vol. of water at 15.4	1.000904

The results of the specific gravity determinations at 0° compared with water at 4° are:—

Determination I	1.54179
Determination II	1.54170

Dr. Thorpe obtained 1.5439 and 1.5466, but was disposed to give the former number double the weight of the latter, as it was made upon a larger quantity of the liquid obtained from a much larger preparation.

56 PASSAVANT ON THE SPECIFIC VOLUME OF CHLORAL.

Both our numbers differ very widely from that obtained by Kopp, viz., 1·5183.

The determination of the rate of expansion was made in one of the dilatometers employed by Dr. Thorpe; this was filled and heated in the arrangement described in his memoir.

The results are as follows:—

Air-therm. degrees.	Observed vol.	Calculated vol.
0·0	2904·14	2903·997
9·63	2934·19	2934·75
17·57	2960·10	2960·63
26·22	2989·22	2989·43
35·26	3020·60	3020·63
44·30	3052·18	3052·53
52·30	3080·92	3081·54
61·14	3113·93	3114·53
70·12	3149·10	3149·079
78·91	3183·56	3183·98

No observations could be taken beyond 79°, owing to the formation of a bubble of gas in the liquid. These numbers lead to the formula—

$$2903·997 + 3·155102t + 0·0038007t^2 + 0·0000149631t^3,$$

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

$$V = 1 + 0·001109498t + 0·0000013338t^2 + 0·0000000051827t^3.$$

By means of the formula the volumes of chloral at every 5° between 0° and 100° have been calculated, on the assumption that this expression correctly represents the expansion between these limits:—

Δ	Volume.	Difference.
0	100000	—
5	100558	558
10	101123	565
15	101696	573
20	102276	580
25	102865	589
30	103463	598
35	104069	606
40	104685	616
45	105310	625
50	105946	636
55	106592	646
60	107249	657
65	107918	669

Δ	Volume.	Difference.
70	108598	680
75	109290	692
80	109995	705
85	110713	718
90	111444	731
95	112188	744
100	112947	759

This formula agrees fairly well with that calculated by Dr. Thorpe from his observations, but is quite different from that of Kopp (*Annalen*, **95**, 307), as will be evident from the following comparison:—

	20°.	40°.	60°.
L. M. P.	10228	10469	10725
Thorpe	10226	10462	10717
Kopp	10187	10385	10615

The relative volume of chloral at its boiling point (97.73°) is 1.12602, as calculated from my observations. Hence its specific gravity at this temperature is $\frac{1.54179}{1.12602} = 1.3692$ compared with water at 4° , and accordingly its specific volume is $\frac{147.01}{1.3692} = 107.37$.

This number agrees almost exactly with that calculated by means of the final values deduced by Dr. Thorpe from his observations, viz., 107.8 ($C = 11$, $Cl = 22.7$, $H = 5.5$, $O = 12.2$), and shows that the oxygen-atom in chloral has precisely the same value that it has in aldehyde.
