# Specific Volume of Camphor and of Borneol determined with proximate accuracy.

By

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The materials employed in the experiments were ordinary commercial camphor and borneol, purified by repeated sublimation. Their melting and boiling points* were found to be as follows :

| | Melt. point. | Boil. point. |
|---|---|---|
| Camphor | 177.7° | 205.3° |
| Borneol | — | 209.7° |

In these determinations a number of experiments were repeated and in each necessary corrections were made.

The determination of the specific gravity of liquid camphor and of liquid borneol was made with the use of a cylindrical specific gravity bottle of a small size whose capacity had carefully been ascertained by filling it with boiled distilled water. Either the camphor or the borneol was fused in a long cylindrical vessel over the paraffin bath, and the specific gravity bottle and its stopper, tied separately with platinum wire, were both introduced into this cylindrical vessel and heated together with the melted camphor or borneol. As the boiling point of the liquid camphor and of the liquid borneol is always found a few degrees higher than that of the vapour, the

* In most text-books the melting and boiling points of camphor are given to be 174° and 204° respectively, and the boiling point of borneol to be 212°.

moment the temperature of the liquid reached 205.3° or 207.9° (boiling points of their vapours), the stopper was instantly closed and the bottle filled with the liquid was taken out, cooled and weighed. These experiments were conducted under a higher barometric pressure than the normal, all the measurements being made by means of the corrected thermometer. The specific gravity was calculated according to the following formula referring to the water of 4°.

$$\text{Specific gravity} = \frac{W}{V(1+3\beta\,(T-t))}$$

$W$ = Weight of the liquid camphor or borneol at $T$.

$T$ = Boiling point of camphor or borneol.

$V$ = Volume of water at $t$ (or the capacity of the bottle at $t$).

$t$ = Temperature when the bottle filled with water was weighed.

$3\beta$ = Coefficient of the cubical expansion of glass = 0.0000254.

## I. Experiments on Camphor $C_{10}H_{16}O$

The following three experiments were performed with a bottle of the capacity of 6.28114 c.c. at 30.5°.

(1) Camphor in the bottle weighed 5.1304 grms at 205.3°.

(2) „ „ „ „ „ 5.1089 „ „ „

(3) „ „ „ „ „ 5.1189 „ „ „

The fourth experiment was performed with a bottle of the capacity of 2.98632 c.c. at 40.5°.

(4) Camphor in the bottle weighed 2.4252 grms at 205.3°.

Seven more experiments were performed with a bottle of the capacity of 2.74518 c.c. at 40.5°.

(5) Camphor in the bottle weighed 2.2400 grms at 205.3°.

(6) Camphor in the bottle weighed 2.2470 grms at 205.3°.
(7) ,, ,, ,, ,, ,, 2.2405 ,, ,, ,,
(8) ,, ,, ,, ,, ,, 2.2330 ,, ,, ,,
(9) ,, ,, ,, ,, ,, 2.2355 ,, ,, ,,
(10) ,, ,, ,, ,, ,, 2.2290 ,, ,, ,,
(11) ,, ,, ,, ,, ,, 2.2315 ,, ,, ,,

Specific gravity at 205.3° deduced according to the formula given above:

| | | | |
|---|---|---|---|
| (1) | 0.8131 | (7) | 0.8127 |
| (2) | 0.8097 | (8) | 0.8100 |
| (3) | 0.8113 | (9) | 0.8109 |
| (4) | 0.8087 | (10) | 0.8085 |
| (5) | 0.8125 | (11) | 0.8094 |
| (6) | 0.8147 | Mean..... | 0.8110 |

$$\text{Specific volume} = \frac{\text{Molec. wt}}{\text{Sp. gravity}} = \frac{152}{0.811} = 187.42$$

## II. Experiments on Borneol $C_{10}H_{18}O$

The experiments were performed with a bottle of the capacity of 2.74518 c.c. at 40.5°.

(1) Borneol in the bottle weighed 2.2284 grms at 209.7°.
(2) ,, ,, ,, ,, ,, 2.2284 ,, ,, ,,
(3) ,, ,, ,, ,, ,, 2.2265 ,, ,, ,,
(4) ,, ,, ,, ,, ,, 2.2245 ,, ,, ,,
(5) ,, ,, ,, ,, ,, 2.2390 ,, ,, ,,
(6) ,, ,, ,, ,, ,, 2.2258 ,, ,, ,,

Specific gravity at 209.7°.

| | | | |
|---|---|---|---|
| (1) | 0.8082 | (4) | 0.8071 |
| (2) | 0.8082 | (5) | 0.8120 |
| (3) | 0.8075 | (6) | 0.8073 |

Mean..... 0.8083

$$\text{Specific volume} = \frac{\text{Molec. wt}}{\text{Sp. gravity}} = \frac{154}{0.8083} = 190.5$$

Specific volume of camphor and of borneol calculated with Kopp's values of the atomic volumes of carbon, hydrogen and oxygen, supposing the former as a ketone and the latter as an alcohol, is found to be as follows:

| Camphor. | | Borneol. | |
|---|---|---|---|
| $C_{10}$ ..... | $10 \times 11 = 110$ | $C_{10}$ ..... | $10 \times 11 = 110$ |
| $H_{16}$ ..... | $16 \times 5.5 = 88$ | $H_{18}$ ..... | $18 \times 5.5 = 99$ |
| O ..... | $1 \times 12.2 = 12.2$ | O ..... | $1 \times 7.8 = 7.8$ |
| Specific volume ..... | 210.2 | ..... | 216.8 |

Thus it is seen that the calculated values are much greater than those found by experiments. Also the specific volume of benzene and of some of its derivatives calculated with Kopp's values is often found to be much greater than those obtained experimentally. In Watt's Dictionary of Chemistry, 3rd Supplement, page 2126, the following statements are given, "Lothar Meyer makes H=3 and Löschmidt C=14 and H=3.5; 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 3.5, we obtain a value for this hydrocarbon which is identical with the observed values." Thus:

| Calculated. | | Found. | |
|---|---|---|---|
| | | Kopp | Ramsay |
| $C_3$ ..... $3 \times 14 = 42$ | | | |
| $C_3$ ..... $3 \times 11 = 33$ | 96 | 95.8 | 95.9 |
| $H_6$ ..... $6 \times 3.5 = 21$ | | | |

I tried to apply these values of carbon and hydrogen and Kopp's values of oxygen (12.2 and 17.8) to camphor and borneol, supposing each to consist of a closed chain of six carbon atoms like benzene, and I found that the calculated specific volumes are almost concordant with those observed.

| Camphor. | | Borneol. | |
|---|---|---|---|
| Calculated | Found | Calculated | Found |
| $C_3 = 3 \times 14$<br>$C_3 = 7 \times 11$<br>$H_{16} = 16 \times 3.5$<br>$O = 1 \times 12.2$ | 187.2 | $C_3 = 3 \times 14$<br>$C_7 = 7 \times 11$<br>$H_{18} = 18 \times 3.5$<br>$O = 1 \times 7.8$ | 189.8 |

I tried farther to compute the specific volumes of some of the benzene derivatives whose experimental numbers are already known, by applying similar method of calculation to them, thus:

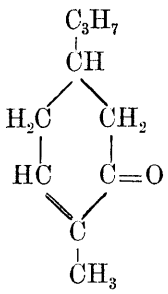
| | Found. | | | Calculated. | |
|---|---|---|---|---|---|
| | Kopp | Ramsay | Yoshida | C=14 & 11; H=3.5; O=12.2 & 7.8 | C=11; H=5.5; O=12.2 & 7.8 |
| Benzene ... ... | 95.8 | 95.9 | — | 96.0 | 99.0 |
| Phenol ... ... | 103.6 | 106.9 | — | 103.8 | 106.9 |
| Benzylalcohol . | 123.7 | — | — | 121.8 | 128.8 |
| Benzaldehyde . | 118.4 | — | — | 119.2 | 122.2 |
| Ethyl benzoate | 172.4–174.8 | — | 163.1* | 162.0 | 174.0 |
| Benzoic acid... | 126.9 | — | — | 127.0 | 130.0 |
| Naphthalene... | 149.2 | — | — | 150.0 | 154.0 |

* This number was observed according to Ramsay's method by Mr. H. Yoshida, Science College, Imperial University of Tokio.

It thus appears that the numbers found by the new way of calculation agree better with the observed ones, in some cases, than with those calculated with Kopp's values.

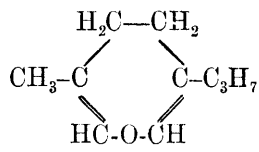
Now the principal formulæ for camphor suggested by different chemists are six in number, namely:

(1)



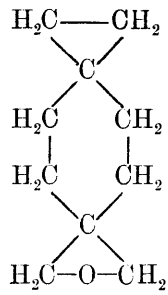
Kekulé.

(2)



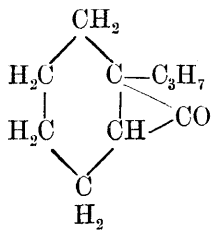
Victor Meyer.

(3)



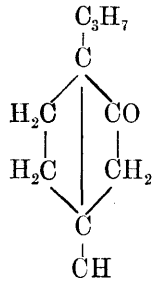
Hlasiwetz.

(4)



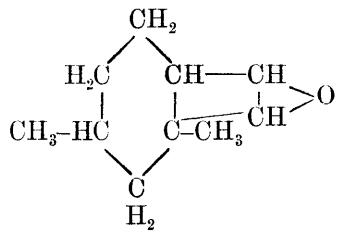
Kachler.

(5)



Kanonnikow.

(6)



Armstrong.

If we suppose the above method of calculation to be true there may exist in camphor, a closed chain of six carbon atoms and

(1) Ber. d. deut. chem. Gesell. VI - 929.
(2) „ „ „ „ „ III - 116.
(3) „ „ „ „ „ III - 540.
(4) Annalen d. Chem. CLXV - 185.
(5) Ber. d. deut. chem. Gesell. XVI - 3051.
(6) „ „ „ „ „ „ XI - 1698.

camphor itself may be a ketone, and then the formula 1, 4 or 5 may represent its constitution, as any one of the remaining formulæ would represent it as an oxide. Kanonnikow,* however, who determined the refraction equivalent of camphor and of its allied compounds by applying Bruhl's method, states that camphor has no double union between carbon atoms. Hence it may be concluded that one of the formulæ 4 and 5 represents the constitution of camphor, and borneol is its corresponding alcohol.

* Ber. d. deut. chem. Gesell. XVI-3051.