[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF WARSAW.]

THE RESTATEMENT AND CORRECTION OF THE THERMO-CHEMICAL DATA ON ORGANIC COMPOUNDS. I. THE DATA OF P. W. ZUBOW.¹

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In 1917 I published in This Journal, a discussion of the necessity of accepting and introducing a standard unit into the thermochemistry of organic compounds, with a view to the correction of all measurements performed by means of the calorimetric bomb.

Before this standard unit should be accepted and established by an authoritative body, I proposed, for the determination of the constant of a calorimetric bomb, the combustion of the following substances and the acceptance of the following heats of combustion:

| Naphthalene | 9612 cal. | Expressed in 15° cal. |
|--------------|-----------|----------------------------|
| Benzoic acid | 6311 cal. | For r g. of substance |
| Cane sugar | 3945 cal. | Weight in air (v-constant) |

The above-mentioned paper states the reasons for accepting these numbers as the most probable. The heat of combustion of naphthalene especially can be considered as very exactly measured, because the determinations performed in 2 different laboratories (in the Bureau of Standards at Washington by Mr. Dickinson, and in the Louginine's Thermochemical Laboratory by myself) had given the identical values of 9612 cal. $\pm 0.01\%$. It is also very probable that 2 other values, 6311 and 3945, are correct within $\pm 0.05\%$. If we accept the cited data as a provisional basis for the thermochemistry of organic compounds, we can then set about to correct the thermochemical data of previous investigators. This problem cannot be deferred, because at present we are already lost in conjectures about the conditions which might have influenced the M. Berthelot's, W. Louginine's, Stohmann's, and all other previous investigators' measurements.

I Note by P. W. Zubow:

[&]quot;I pointed out formerly that the values given by my determinations were too large and explained this by the hypothesis that the heat capacity of my bomb had been erroneously determined. To correct my data, I had intended to make a new determination of the heat capacity, but I put off this experiment, believing that my values were comparable with each other, and relatively true and exact. The investigations of W. Swietoslawski have shown that the correction of my data can be performed without a new determination of the heat capacity of the bomb. The correction of my data by means of a constant factor had been often discussed with W. Swietoslawski and when the latter raised the question of introducing a standard unit into thermochemistry and correcting all previous thermochemical data, I expressed my pleasure at his proposal to recalculate my measurements. For this purpose I have delivered to W. Swietoslawski all my experimental data.— P. W. Zubow."

² This Journal, 39, 2595 (1917).

In another paper corrections will be published which ought to be introduced in the measurements of the above mentioned authors. In this communication will be given the corrected data of P. W. Zubow; the results of measurements performed with the greatest accuracy and precision in Louginine's Thermochemical Laboratory at Moscow in 1892–1910.

It is to be noted that the data of Zubow are especially important, because the heat capacity of his apparatus was determined by the same method as that used by M. Berthelot in his first measurements, besides which Zubow's calorimetric bomb was made by Golaz in Paris at the same time as M. Berthelot's bomb, and the constant of the apparatus was determined by the combustion of naphthalene, accepting for the heat of combustion the first data of Berthelot, obtained in 1887. This circumstance is very important, because it will facilitate in the future the solution of several problems, by correcting the earlier thermochemical data.

The correction of Zubow's data does not involve any difficulty, inasmuch as the author has furnished me with all his experimental data, beginning with those of 1892, and has rendered possible in this way the complete reconsideration of the whole question. Moreover the combustion of naphthalene, which was performed by Zubow with the greatest precision, facilitated the computation of the factor necessary for correcting his data.

If we accept 9612 cal. as the heat of combustion of naphthalene, for one gram weighed in air, and consider that Zubow obtained the value 9706 cal. $\pm 0.03\%$, we obtain the factor:

$$\alpha = \frac{9612}{9706} = 0.9907$$

Denoting the heat of combustion as given in Zubow's previous publications by A_{un} , we then obtain as the corrected value A_{cor} .

$$A_{\text{cor.}} = \alpha A_{\text{un.}} = 0.9907 A_{\text{un.}}$$

This value corresponds to the heat of combustion of 1 g. of liquid or solid substance burned at 18°, at constant volume.

In Tables I to VI are given the corrected values for 40 hydrocarbons, 41 alcohols, 23 ketones, 7 esters, 9 acids and 6 compounds containing nitrogen.

In these tables $A_{\rm un}$ indicates Zubow's uncorrected data; $A_{\rm cor.}$, the heat of combustion of one gram of substance weighed in air; $A_{\rm mol}$ (v const. or p const.), the heat of combustion of one mole of substance, weighed in air; $A_{\rm mol~(abs.)}$ —the molecular heat of combustion of substance, weighed in a vacuum; W_{18}^t , the correction for the gaseous state of the substance, when t° indicate the boiling point. The last values were computed from the specific heats c_{18-t} and the heats of evaporation W_t of the substances

TABLE I.—HYDROCARBONS.

| | | | | Aun. | Acor. | Amol. | Amol. | Amol. (ab. (p=const. | s.) [XZ] | Agas. | |
|-----|---------------|---------------------------------|--------|------------|------------|------------|---------------|----------------------|----------|---------|---------|
| No. | Formula. | Name. | M. | (r∞const.) | (v=const.) | (v=const.) | (p=const.) | (p=const. |) M 18 | (p=cons | t.) No. |
| 1 | C_5H_{10} | Trimethyl-ethylene | 70.08 | 11466.3 | 11355.1 | 795.8 | $797 \cdot 3$ | 796.0 | 7.2 | 803.2 | ĭ |
| 2 | C_5H_{10} | Methyl-cyclobutane | 70.08 | 11293.1 | 11183.6 | 783.7 | 785.2 | 784.2 | 7.9 | 792.I | 2 |
| 3 | C_5H_{10} | Cyclopentane | 70.08 | 11284.1 | 11174.6 | 783.1 | 784.6 | 783.6 | 7.9 | 791.5 | 3 |
| 4 | C_6H_8 | Dihydro-benzene | 80.06 | 10506.9 | 10405.0 | 833.0 | 834.2 | 833.2 | 9.9 | 843.1 | 4 |
| 5 | C_6H_{10} | Dimethyl-methylene-cyclopropane | 82.08 | 11043.7 | 10936.6 | 897.7 | 899.2 | 898.0 | 8.9 | 906.9 | 5 |
| 6 | C_6H_{10} | Cyclohexene | 82.08 | 10962.0 | 10855.7 | 891.0 | 892.5 | 891.2 | 9.7 | 900.9 | 6 |
| 7 | $C_{5}H_{12}$ | Methyl-cyclopentane | 84.10 | 11258.2 | 11149.0 | 937.6 | 939:3 | 937.9 | 9.5 | 947 - 4 | 7 |
| 8 | C_6H_{12} | Cyclohexane | 84.10 | 11237.4 | 11128.4 | 935.9 | 937.6 | 936.3 | 9.9 | 946.2 | 8 |
| 9 | C_6H_{12} | Hexylene | 84.10 | 11435.2 | 11324.3 | 952.4 | 954.1 | 952.6 | 9.3 | 961.9 | 9 |
| 10 | C_6H_{14} | n-Hexane | 86.11 | 11602.6 | 11490.0 | 989.4 | 991.4 | 989.8 | 8.7 | 998.5 | 10 |
| 11 | C_7H_{12} | Methyl-1-cyclohexene-1 | 96.10 | 10935.8 | 10829.7 | 1040.7 | 1042.4 | 1040.9 | 12.7 | 1053.6 | 11 |
| 12 | C_7H_{12} | Methyl-1-cyclohexene-3 | 96.10 | 10963.0 | 10856.7 | 1043.3 | 1045.0 | 1043.6 | 12.3 | 1055.9 | 12 |
| 13 | C_7H_{12} | Methylene-cyclohexane | 96.10 | 10967.8 | 10861.4 | 1043.8 | 1045.5 | 1044.1 | 12.5 | 1056.6 | 13 |
| 14 | C_7H_{12} | Bicycloheptane | 96.10 | 10928.2 | 10822.2 | 1030.0 | 1031.7 | 1030.3 | 12.2 | 1042.5 | 14 |
| 15 | C_7H_{12} | Cycloheptene | 96.10 | 11028.2 | 10921.2 | 1049.5 | 1051.3 | 1049.9 | 13.1 | 1063.0 | 15 |
| 16 | C_7H_{14} | 1,3-Dimethyl-cyclopentane | 98.11 | 11219.4 | 11110.6 | 1091.1 | 1092.1 | 1090.7 | 11.4 | 1102.1 | 16 |
| 17 | C_7H_{14} | Methyl-cyclohexane | 98.11 | 11233.0 | 11124.0 | 1091.4 | 1093.4 | 8.1001 | 12.4 | 1104.2 | 17 |
| 18 | C_7H_{14} | Cycloheptane | 98.11 | 11186.4 | 11077.9 | 1086.9 | 1088.9 | 1087.3 | 13.3 | 1100.6 | 18 |
| 19 | C_8H_{12} | 1,3-Dimethyl-dihydrobenzene | 108.10 | 10724.5 | 10620.5 | 1148.1 | 1149.8 | 1148.2 | 14.5 | 1162.7 | 19 |

| 20 | C_8H_{14} | 1,1,2-Trimethyl-cyclopentene-2 (iso- | | | | | | | | | |
|----|---------------------------------|--------------------------------------|--------|---------|---------|--------|--------|--------|------|--------|----|
| | | laurolene) | 110.11 | 10939.8 | 10833.7 | 1192.9 | 1194.9 | 1193.3 | 13.4 | 1206.7 | 20 |
| 21 | C_8H_{14} | Laurolene | 110.11 | 10934.2 | 10828.1 | 1192.3 | 1194.3 | 1192.7 | 14.3 | 1207.0 | 21 |
| 22 | C_8H_{14} | 1,3-Dimethyl-cyclohexene-3 | 110.11 | 10950.7 | 108.445 | 1194.1 | 1196.1 | 1194.5 | 15.0 | 1209.5 | 22 |
| 23 | C_8H_{16} | 1,2,4-Trimethyl-cyclopentane | 112.13 | 11211.8 | 11103.0 | 1245.0 | 1247.3 | 1245.4 | 13.8 | 1259.2 | 23 |
| 24 | C_8H_{16} | 1,1-Dimethyl-cyclohexane | 112.13 | 11185.5 | 11077.0 | 1242.1 | 1244.4 | | 13.9 | 1256.4 | 24 |
| 25 | C_8H_{16} | 1,3-Dimethyl-cyclohexane | 112.13 | 11144.1 | 11036.0 | 1237.5 | 1239.8 | 1238.0 | 14.4 | 1252.4 | 25 |
| 26 | C_8H_{16} | 1,4-Dimethyl-cyclohexane | 112.13 | 11061.5 | 10954.2 | 1228.3 | 1230.6 | 1228.8 | 14.4 | 1243.2 | 26 |
| 27 | C_8H_{16} | Methyl-cycloheptane | 112.13 | 11203.6 | 11094.9 | 1244.1 | 1246.4 | 1244.5 | 15.7 | 1260.2 | 27 |
| 28 | C_8H_{18} | <i>n</i> -Octane | 114.14 | 11519.9 | 11408.1 | 1302.I | 1304.7 | 1302.7 | 15.0 | 1317.7 | 28 |
| 29 | C_9H_{18} | Methyl-1-n-propyl-cyclopentane | 126.14 | 11213.3 | 11104.5 | 1400.7 | 1403.3 | 1401.4 | 17.5 | 1418.9 | 29 |
| 30 | $\mathrm{C}_{9}\mathrm{H}_{18}$ | 1,2,3-Trimethyl-cyclohexane | 126.14 | 11169.0 | 11060.7 | 1395.2 | 1397.8 | 1395.9 | 17.4 | 1413.3 | 30 |
| 31 | C_9H_{18} | 1,3,3-Trimethyl-cyclohexane | 126.14 | 11159.1 | 11050.9 | 1394.0 | 1396.6 | 1394.7 | 16.8 | 1411.5 | 31 |
| 32 | C_9H_{18} | Ethyl-cycloheptane | 126.14 | 11256.2 | 11147.0 | 1406.1 | 1408.7 | 1406.8 | 19.3 | 1426.1 | 32 |
| 33 | $C_{10}H_{16}$ | l-Limenene | 136.13 | 10806.6 | 10701.8 | 1456.8 | 1459.1 | 1457.2 | 19.4 | 1476.6 | 33 |
| 34 | $C_{10}H_{15}$ | <i>l</i> -Pinene | 136.13 | 10924.5 | 10818.5 | 1472.7 | 1475.0 | 1473.2 | 18.7 | 1491.9 | 34 |
| 35 | $C_{10}H_{10}$ | d-Pinene | 136.13 | 10914.6 | 10808.7 | 1471.4 | 1473.7 | 1471.9 | 18.7 | 1490.6 | 35 |
| 36 | $C_{10}H_{18}$ | Phenchane | 138.14 | 10980.3 | 10873.8 | 1502.1 | 1504.7 | 1502.8 | 19.3 | 1522.1 | 36 |
| 37 | $C_{10}H_{20}$ | Methyl-1-n-propyl-3-cyclohexane | 140.16 | 11168.7 | 11060.4 | 1550.2 | 1553.1 | 1550.9 | 21.9 | 1572.8 | 37 |
| 38 | $C_{10}H_{20}$ | Caromenthane | 140.16 | 10907.0 | 10801.2 | 1513.9 | 1516.8 | 1514.6 | 21.9 | 1536.5 | 38 |
| 39 | $C_{10}H_{22}$ | n-Decane | 142.18 | 11438.8 | 11327.8 | 1610.6 | 1613.8 | 1610.2 | 20.2 | 1630.4 | 39 |
| 40 | $C_{14}H_{26}$ | m-Hexahydro-ditolyl | 194.21 | 10945.7 | 10839.5 | 2105.1 | 2108.9 | 2105.9 | 37.1 | 2143.0 | 40 |

TABLE II.—ALCOHOLS.

| 7.7 | P 1. | 3 * | 3.6 | Aun. | $A_{\rm cor.}$ | A_{mol} . | Amol. | A mel. (abs.) (p =const.) |) _{TX7} t | 4 | |
|-------|-----------------------|------------------------------|--------|------------|----------------|--------------------|-----------|------------------------------|--------------------|------------|-----|
| 1/40. | Formula. | Name. | M. | (v=const.) | (v=const.) | (v=const.) | (p=const. |) (p = const.) | W 18- | $A_{gas.}$ | No. |
| 1 | $\mathrm{C_3H_8O}$ | Propyl alcohol | 60.06 | 8075.7 | 7997 - 4 | 480.3 | 481.2 | 480.5 | 12.8 | 499.3 | 1 |
| 2 | C_3H_8O | iso-Propyl alcohol | 60.06 | 7979.2 | 7901.8 | 474.6 | 475.5 | 474.8 | 12.1 | 486.9 | 2 |
| 3 | $C_4H_{10}O$ | n-Butyl alcohol | 74.08 | 8699.8 | 8615.4 | 638.2 | 639.4 | 638.6 | 15.1 | 653.7 | 3 |
| 4 | $C_4H_{10}O$ | iso-Butyl prim. alcoho | 74.08 | 8662.5 | 8578.5 | 635.5 | 636.7 | 635.8 | 14.6 | 650.4 | 4 |
| 5 | $C_4H_{10}O$ | Trimethyl-carbinol | 74.08 | 8573.8 | 8490.6 | 629.0 | 630.2 | 629.3 | 13.3 | 642.6 | 5 |
| 6 | $C_5H_{10}O$ | Cyclobutyl-carbinol | 86.08 | 8769.6 | 8684.5 | 747.6 | 748.8 | 747.8 | 17.6 | 765.4 | 6 |
| 7 | $C_5H_{12}O$ | Amyl alcohol (ferm.) | 88.10 | 9068.8 | 8980.8 | 791.2 | 792.7 | 791.6 | 16.9 | 808.5 | 7 |
| 8 | $\mathrm{C_5H_{12}O}$ | Dimethyl-ethyl-carbinol | 88.10 | 8986.9 | 8899.7 | 784. I | 785.6 | 784.6 | 14.7 | 799.3 | 8 |
| 9 | $\mathrm{C_6H_{12}O}$ | β-Methyl-cyclopentanol | 100.10 | 8950.6 | 8863.8 | 887.3 | 888.8 | 887.6 | 19.6 | 907.2 | 9 |
| 10 | $C_6H_{12}O$ | Cyclohexanol | 100.10 | 8973.2 | 8886.2 | 889.5 | 891.0 | 889.8 | 20.7 | 910.5 | 10 |
| 11 | $\mathrm{C_6H_{12}O}$ | Allyl-dimethyl-carbinol | 100.10 | 8940.5 | 8853.8 | 886.3 | 887.7 | 886.5 | 16.3 | 902.8 | 11 |
| 12 | $C_6H_{14}O$ | Methyl-diethyl-carbinol | 102,11 | 9162.4 | 9073.5 | 926.5 | 928.2 | 927.0 | 16.5 | 943 - 5 | 12 |
| 13 | $C_6H_{14}O$ | Pinacoline alcohol | 102.11 | 9277.6 | 9187.6 | 938.1 | 939.8 | 938.6 | 16.5 | 955.1 | 13 |
| 14 | $C_7H_{12}O$ | Diallyl-carbinol | 112.10 | 9261.4 | 9171.6 | 1028.1 | 1029.5 | 1028.2 | 21.2 | 1049.4 | 14 |
| 15 | $C_7H_{14}O$ | 1,3-Dimethyl-cyclopentanol-2 | 114.11 | 9115.4 | 9027.0 | 1030.1 | 1031.8 | 1030.5 | 21.3 | 1051.8 | 15 |
| гő | $C_7H_{14}O$ | β -Cyclohexanol | 114.11 | 9186.0 | 9096.9 | 1038.0 | 1039.7 | 1038.4 | 23.6 | 1062.0 | 16 |
| 17 | $C_7H_{14}O$ | Cycloheptanol | 114.11 | 9289.7 | 9199.6 | 1049.8 | 1051.5 | 1050.2 | 24.9 | 1075.1 | 17 |
| 18 | $C_7H_{14}O$ | Ethyl-1-cyclopentanol-2 | 114.11 | 9190.7 | 9101.5 | 1038.6 | 1040.3 | 1039.0 | 24.0 | 1063.0 | 18 |
| 19 | $C_7H_{14}O$ | 1,3-Dimethyl-cyclopentanol-3 | 114.11 | 9146.8 | 9058.1 | 1033.6 | 1035.3 | 1034.0 | 24.0 | 1058.0 | 19 |
| 20 | $C_7H_{14}O$ | Cyclohexyl-carbinol | 114.11 | 9263.4 | 9173.5 | 1046.8 | 1048.5 | 1047.2 | 24.0 | 1071.2 | 20 |

| 2 I | $C_7H_{14}O$ | Allyl-methyl-ethyl-carbinol | 114.11 | 9289.4 | 9199.3 | 1049.7 | 1051.4 | 1050.1 | 19.7 | 1069.8 | 21 |
|------------|--|------------------------------------|--------|--------|--------|--------|--------|--------|------|--------|----|
| 22 | $C_7H_{16}O$ | n-Heptyl alcohol | 116.13 | 9602.8 | 9509.7 | 1104.4 | 1106.4 | 1104.9 | 24.2 | 1129.1 | 22 |
| 23 | $C_7H_{16}O$ | Triethyl-carbinol | 116.13 | 9385.4 | 9294.4 | 1079.4 | 1081.4 | 1080.0 | 20.0 | 1100.0 | 23 |
| 24 | $C_8H_{14}O$ | Diallyl-methyl-carbinol | 126.11 | 9452.3 | 9360.6 | 1180.5 | 1182.2 | 1180.7 | 23.0 | 1203.7 | 24 |
| 25 | $C_8H_{16}O$ | 1,3-Dimethyl-cyclohexanol-2 | 128.13 | 9421.9 | 9330.5 | 1195.5 | 1197.5 | 1196.0 | 25.7 | 1221.7 | 25 |
| 26 | $C_8H_{16}O$ | 1,3-Dimethyl-cyclohexanol-5 | 128.13 | 9321.4 | 9231.0 | 1182.8 | 1184.8 | 1183.4 | 26.9 | 1210.3 | 26 |
| 27 | $C_8H_{16}O$ | Allyl-methylpropyl-carbinol | 128.13 | 9468.8 | 9377.0 | 1201.5 | 1203.5 | 1201.9 | 22.9 | 1224.8 | 27 |
| 28 | $C^8H^{16}O$ | Allyl-diethyl-carbinol | 128.13 | 9509.5 | 9417.3 | 1206.6 | 1208.6 | 1207.1 | 22.9 | 1230.0 | 28 |
| 29 | $C_8H_{16}O$ | 1,3-Dimethyl-cyclohexanol-3 | 128.13 | 9394.3 | 9303.2 | 1192.0 | 1194.0 | 1192.5 | 26.6 | 1219.1 | 29 |
| 30 | $C_8H_{16}O$ | Methyl-1-cycloheptanol | 128.13 | 9370.0 | 9279.I | 1188.9 | 1190.9 | 1189.4 | 26.6 | 1216.0 | 30 |
| 31 | $C_8H_{18}O$ | Methyl-dipropyl-carbinol | 130.14 | 9559.6 | 9466.9 | 1232.0 | 1234.4 | 1232.7 | 23.7 | 1256.4 | 31 |
| 32 | $C_9H_{16}O$ | 1,3,5-Trimethyl-cyclohexene-6-ol-5 | 140.13 | 9327.9 | 9237.4 | 1294.4 | 1296.4 | 1294.7 | 30.0 | 1324.7 | 32 |
| 33 | $C_9H_{18}O$ | Methylethyl-1,3-cyclohexanol-3 | 142.14 | 9390.7 | 9299.6 | 1321.8 | 1324.1 | 1322.4 | 30.0 | 1352.4 | 33 |
| 34 | $C_9H_{18}O$ | Cycloheptyl-methyl-carbinol | 142.14 | 9530.7 | 9438.3 | 1341.6 | 1343.9 | 1349.2 | 29.4 | 1371.6 | 34 |
| 3 5 | $C_9H_{18}O$ | n-Allylmethyl-n-butylcarbinol | 142.14 | 9692.4 | 9598.4 | 1364.3 | 1366.6 | 1364.9 | 27.7 | 1392.6 | 35 |
| 36 | $C_9H_{18}O$ | Allylmethyl-tert-butylcarbinol | 142.14 | 9679.1 | 9585.2 | 1362.4 | 1364.7 | 1363.0 | 26.1 | 1389.1 | 36 |
| 37 | $\mathrm{C_9H_{20}O}$ | Ethyl-dipropyl-carbinol | 144.16 | 9705.3 | 9611.2 | 1385.6 | 1388.2 | 1386.5 | 27.8 | 1414.3 | 37 |
| 38 | $C_{10}H_{18}O$ | Diallyl-propyl-carbinol | 154.14 | 9640.7 | 9547.2 | 1471.6 | 1473.9 | 1472.1 | 31.2 | 1503.3 | 38 |
| 39 | $\mathrm{C}_{10}\mathrm{H}_{20}\mathrm{O}$ | Allyl-dipropyl-carbinol | 156.16 | 9811.1 | 9715.9 | 1517.2 | 1519.9 | 1518.0 | 31.3 | 1549.3 | 39 |
| 40 | $\mathrm{C}_{11}\mathrm{H}_{22}\mathrm{O}$ | Allyl-methylhexyl-carbinol | 170.18 | 9884.3 | 9788.4 | 1665.8 | 1668.7 | 1666.7 | 35.8 | 1702.5 | 40 |
| 41 | $C_5H_{10}O_2$ | Dimethylol-cyclopropane | 102.08 | 7002.4 | 6934.5 | 707.9 | 708.8 | 707.6 | | | 41 |

TABLE III.—KETONES.

| No. | Formula. | Name. | M. | A _{un.} | $A_{\text{cor.}}$ $(v=\text{const.})$ | $A_{\text{mol.}}$ $(v=\text{const.})$ | $A_{\text{mol.}}$ (p =const.) | Amol. (abs (p=const.) | W_{19}^{t} | Agas. · (p=cons | t.) No. |
|-----|-----------------------|-------------------------------------|--------|------------------|---------------------------------------|---------------------------------------|-------------------------------------|--------------------------|--------------|-----------------|---------|
| I | C_4H_8O | Methylethyl-ketone | 72.06 | 8158.1 | 8079.0 | 582.2 | 583.1 | 582.3 | 9.8 | 592.1 | 1 |
| 2 | C_5H_8O | Acetyl-trimethylene | 84.06 | 8303.4 | 8222.9 | 691.2 | 692.1 | 691.4 | 11.5 | 702.9 | 2 |
| 3 | $C_5H_{10}O$ | Methylpropyl-ketone | 86.08 | 8615.5 | 8531.9 | 734 · 4 | 736.5 | 734.6 | 11.5 | 746. I | 3 |
| 4 | $C_5H_{10}O$ | Methyl-iso-propyl-ketone | 86.08 | 8607.2 | 8523.7 | 733.7 | 734.9 | 733.9 | 11.0 | 744.9 | 4 |
| 5 | $C_5H_{10}O$ | Diethyl-ketone | 86.08 | 8627.0 | 8543.3 | 735 - 4 | 736.6 | 735.6 | 11.7 | 747.3 | 5 |
| 6 | $\mathrm{C_6H_{10}O}$ | β -Methyl-cyclopentanone | 98.08 | 8578.6 | 8495.4 | 833.2 | 834.4 | 833.4 | 15.4 | 848.8 | 6 |
| 7 | $\mathrm{C_6H_{10}O}$ | Acetyl-cyclobutane | 98.08 | 8818.7 | 8733.2 | 856.6 | 857.8 | 856.8 | 14.9 | 871.7 | 7 |
| 8 | $\mathrm{C_6H_{12}O}$ | Methylbutyl-ketone | 100.10 | 9027.9 | 8940.3 | 894.9 | 896.4 | 895.2 | 14.2 | 909.4 | 8 |
| 9 | $C_6H_{12}O$ | tert-Methylbutyl-ketone | 100.10 | 8993.5 | | 891.5 | 893.0 | 891.8 | 13.0 | 904.8 | 9 |
| 10 | $C_7H_{12}O$ | β-Methyl-cyclohexanone | 112.10 | 8958.8 | 8871.9 | 994.5 | 996.0 | 994.8 | 18.9 | 1013.7 | 10 |
| 11 | $C_7H_{12}O$ | Cycloheptanone (Suberon.) | 112.10 | 8974.3 | 8887.2 | 996.3 | 997.8 | 996.7 | 19.9 | 1016.6 | 11 |
| 12 | $C_7H_{12}O$ | Ethyl-1-cyclopentanone-2 | 112.10 | 8918.8 | 8832.3 | 990.1 | 991.6 | 990.4 | 18.2 | 1008.6 | 12 |
| 13 | $C_7H_{12}O$ | 1,3-Dimethyl-cyclopentanone-2 | 112.10 | 8913.1 | 8826.6 | 989.5 | 991.0 | 989.8 | 16.8 | 1006.6 | 13 |
| 14 | $C_7H_{14}O$ | Dipropyl-ketone | 114.11 | 9293.3 | 9203.2 | 1050.2 | 1051.9 | 1050.5 | 16.4 | 1066.9 | 14 |
| 15 | $C_8H_{12}O$ | 1,3-Dimethyl-cyclohexene-6-one-5 | 124.10 | 8966.3 | 8879.3 | 1101.9 | 1103.4 | 1102.2 | 24.2 | 1126.4 | 15 |
| 16 | $C_8H_{14}O$ | 1,3-Dimethyl-cyclohexanone-2 | 126.11 | 9043.8 | 8956.1 | 1129.5 | 1131.2 | 1129.8 | 20.7 | 1150.5 | 16 |
| 17 | $C_8H_{16}O$ | Methylhexyl-ketone | 128.13 | $9494 \cdot 3$ | 9402.2 | 1204.7 | 1206.7 | 1205.1 | 20.3 | 1225.4 | 17 |
| 18 | $C_9H_{14}O$ | 1,1,5-Trimethyl-cyclohexene-5-one-3 | 138.11 | 9124.9 | 9036.4 | 1248.0 | 1249.7 | 1248.4 | 26.4 | 1274.8 | 18 |
| 19 | $\mathrm{C_9H_{16}O}$ | 1,4-Methylacetyl-cyclohexanone | 140.11 | 9134.1 | 9045.5 | 1267.4 | 1269.4 | 1267.8 | 24.2 | 1292.0 | 19 |
| 20 | $C_9H_{16}O$ | Ethyl-cyclohexyl-ketone | 140.11 | 9290.8 | 9200.7 | 1289.1 | 1291.1 | 1289.5 | 24.2 | 1313.7 | 20 |
| 21 | $C_9H_{16}O$ | Methyl-cycloheptyl-ketone | 140.11 | 9209.9 | 9120.6 | 1277.9 | 1279.9 | 1278.3 | 24.2 | 1302.5 | 2 1 |
| 22 | $C_{10}H_{16}O$ | Dihydrocarvone | 152.11 | 9373 - 3 | 9282.4 | 1411.9 | 1413.9 | 1412.2 | 29.7 | 1441.9 | 22 |
| 23 | $C_{10}H_{16}O$ | Carone | 152.11 | 9271.1 | 9181.2 | 1396.6 | 1398.6 | 1397.1 | 27.6 | 1424.7 | 23 |

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| NG. | Formula. | | M. | | | | | | | | |
|-----|-------------------------|---|----------|-------------------|-------------------|-----------------|--------------------|--|---------|----------------------------|----------|
| | | Dimethyl-carbonate | 90.05 | - | 3787.4 | 341.1 | 341.I | Amol. (abs.) (p=const.) 340.8 | ro.8 | A _{gas.} 351.6 | No. I |
| 2 | $C_5H_{10}O_2$ | Diethyl-carbonate | 118.08 | 5540.9 | 5487.2 | 647.9 | 648.5 | | 14.5 | 662.4 | 2 |
| | $C_6H_{10}O_2$ | Methylester of cyclobutane acid | 114.08 | | 7091.6 | 809.0 | 809.9 | | 15.8 | 824.9 | |
| 3 | | Ethylester of methylethyl-1,4-cyclopen- | 114.00 | /101.1 | 7091.0 | 009.0 | 009.9 | 009.1 | 13.0 | 024.9 | 3 |
| 4 | C101116O3 | tane acid | **** | m 160 m | =a06 a | 7.46° ° | 7.67 A | - 46- 9 | | | |
| _ | C II O | | 198.14 | | 7396.3 | | 1467.2 | 1465.8 | • • | • • | 4 |
| 5 | | Tricyclobutyrine | 296.16 | - | 6230.6 | 1845.3 | 1846.5 | 1844.9 | • • | • • | 5 |
| 6 | $C_{15}H_{26}O_6$ | - | 302.21 | 6485.3 | 6422.4 | | 1942.9 | 1941.1 | • • | • • | 6 |
| 7 | $C_{18}H_{26}O_6$ | Tricyclo-valerine | 338.21 | 6892.8 | 6825.9 | 2308.6 | 2310.6 | 2308.6 | • • | • • | 7 |
| | | | TABLE V | .—Acms. | | | | | | | |
| | | | | $A_{\mathbf{un}}$ | Acor. (v=const.) | $A_{\rm mol}$. | $A_{ m mol}$. | Amol. (abs. |) TA7t | | |
| No. | Formula. | | М. | | | | | | | $A_{ m gas.}$ | No. |
| I | $C_4H_6O_2$ | Trimethylene-carbon acid | 86.05 | 5677.6 | 5622.5 | 483.8 | 484.1 | 483.7 | 17.3 | 501.0 | 1 |
| 2 | $\mathrm{C_5H_8O_2}$ | Cyclobutane-carbon acid | 100.06 | 6450.8 | 6388.3 | 639.2 | 639.8 | 639.2 | 19.9 | 659.1 | 2 |
| 3 | $\mathrm{C_6H_{12}O_2}$ | Capric acid (act.) | 116.10 | 7225.6 | 7155.5 | 830.8 | 832.0 | 831.0 | 21.5 | 852.5 | 3 |
| 4 | $\mathrm{C_6H_{12}O_2}$ | Acid from the chloride of russian benzine | 116.10 | 7226.6 | 7156.5 | 830.9 | 832.1 | 831.1 | 21.5 | 852.6 | 4 |
| 5 | $\mathrm{C_7H_{12}O_2}$ | Cyclohexane-carbon acid | 128.10 | 7361.4 | 7290.0 | 933.8 | 935.0 | 934.0 | | | 5 |
| 6 | $C_8H_{14}O_2$ | Hexahydro-m-tolyl acid | 142.11 | 7715.5 | 7640.7 | 1085.8 | 1087.3 | 1086.2 | | | 6 |
| 7 - | $C_8H_{14}O_2$ | Cyclo-octane acid (act.) | 142.11 | 7736.9 | 7661.9 | 1088.8 | 1090.3 | 1089.2 | | | 7 |
| 8 | $C_8H_{14}O_2$ | Acid from benzine, 100–102° | 142.11 | 7683.9 | 7609.4 | 1081.4 | 1082.9 | 8.1801 | | | 8 |
| 9 | $C_8H_{14}O_2$ | Cycloheptane-carbon acid | 142.11 | 7720.3 | 7645.4 | 1086.5 | 1088. о | 1087.9 | | | 9 |
| | | Table VI.—I | Nitrogen | CONTAIN | ung Subs | TANCES. | | | | | |
| | | | | A_{un} . | $A_{\text{cor.}}$ | $A_{ m mol}$. | A_{mol} . | $A_{\text{mol.}}$ (abs) ($p = const.$ | .) 1771 | | |
| No. | Formula. | | M. | (v=const.) | (v=const.) | (v=const.) | | |) W 18. | | No. |
| 1 | C_4H_9ON | Methylethyl-ketoxime | 87.08 | 7497 · 5 | 7424.8 | 646.6 | 647.3 | 646.5 | 17.5 | 664.0 | I |
| 2 | $C_9H_{17}ON$ | Cyclo-heptylmethyl-ketoxime | 155.15 | 8873.1 | 8787.0 | 1363.3 | 1365.2 | 1363.5 | | | 2 |
| 3 | $C_5H_{11}N$ | 1,1-Amino-cyclopropyl-ethane | 85.10 | 9767.2 | 9672.5 | 823.1 | 824.4 | 823.3 | 11.1 | 834.4 | 3 |
| 4 | $C_7H_{15}N$ | 1-Methyl-cyclohexyl-amine-3 | 113.13 | 9982.0 | 9885.2 | 1118.3 | 1120.2 | 1118.7 | 16.8 | 1135.5 | 4 |
| 5 | $C_9H_{19}N$ | Cycloheptyl-methylamino-methane | 141.16 | 10213.6 | 10114.5 | 1427.8 | 1430.3 | 1428.4 | 22.I | 1450.5 | 5 |
| 6 | $C_6H_{12}N$ | Dimethyl-4,4-tetrahydro-furane | 100.10 | 9059.2 | 8971.3 | 898.0 | 899.5 | 898.5 | 11.7 | 910.2 | 6 |

at t° . Where the experimental data for this computation were not known, the values for W_{18}^{t} were interpolated. $A_{\rm gas.}$ indicates the molecular heat of combustion of the substances in the gaseous state at t° and $p = {\rm const.}$

A comparison of Zubow's data with those of other authors will be made in the next paper.

WARSAW, POLAND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE CRYSTAL STRUCTURE OF CESIUM DICHLORO-IODIDE.1

By RALPH W. G. WYCKOFF. Received March 1, 1920.

Purpose of the Investigation.—The crystal structure of the alkali halides, sodium and potassium chlorides, has been determined.² It has seemed of particular interest to ascertain the modifications in this structure which result when more halogen atoms are introduced into the molecule with the formation of alkali polyhalides.

The real nature of these compounds has long been in doubt and it was felt that a knowledge of the crystal structure of a typical polyhalide might aid in removing this uncertainty. Formerly it was customary to consider these compounds as "double salts" or "addition compounds," for instance the trihalides as compounds of RX and XX'(CsCl·ICl) where R is an alkali metal and X and X' are halogens, and the pentahalides as compounds of RX and XX'₈(CsCl·ICl₃). The ease with which such compounds as R(ICl₄) are decomposed into normal halide and complex halogen (RCl and ICl₃) by carbon tetrachloride supported this view. By some the halogen atoms were considered to be grouped about the positive atom but as Werner has pointed out, this point of view is quite untenable. The view which seems to agree best with the properties of these compounds considers them to be compounds of metal ion or group and complex halogen anion. More recent studies, especially upon the polyiodides, have strengthened this view.

Cesium dichloro-iodide (CsCl₂I) was chosen for this study of crystal structure because of its supposed dimorphism, and because experience had shown that good crystals of one of these forms at least could be readily prepared.

- ¹ This article is based upon a portion of the thesis presented to the Faculty of the Graduate School of Cornell University by Ralph W. G. Wyckoff in partial fulfilment of the requirements for the degree of Doctor of Philosophy.
 - ² W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," 1918. Chap. VII.
- 3 Wells and Penfield, $Am.\ J.\ Sci.$, [3] 43, 29 (1892) discuss possible structures for the trihalides.
 - ⁴ Weinland and Schlegelmilch, Z. anorg. Chem., 30, 134 (1902).
 - ⁵ A. Werner, "New Ideas on Inorganic Chemistry" (Hedley, translator), 1911, p. 86.
- 6 R. Abegg u. F. Auerbach, "Handbuch d. anorg. Chem.," Bd. IV, Abt., 2, 432 et seq. (1913).