

CALORIMETRIC RESEARCHES

BY

P. E. VERKADE, H. HARTMAN AND J. COOPS.

X. Heats of combustion of successive terms of homologous series: Dicarboxylic acids of the oxalic acid series¹⁾.§ 1. *Introduction.*

Thanks to improvements in the apparatus and in the method of measurement we are now in a position to determine heats of combustion of organic substances with an accuracy which greatly surpasses that obtainable only a few years ago; we are of the opinion that, *if for some reason or other it should be desired*, an accuracy of about 0.1 per thousand should be attainable, of course provided that the properties of the substance under investigation are not opposed to this. At the same time, the technique of preparing organic compounds has advanced considerably, due to no small degree to the introduction of catalytic methods; in very many cases organic compounds may now be obtained much more easily and in a much purer condition than heretofore. In the light of these facts it is obvious that it may be profitable to take up again problems concerning the relationship between constitution and heat of combustion of organic compounds, which have already been treated experimentally, — be it often only very superficially — by previous investigators. *That relating to the heats of combustion of successive terms of homologous series* belongs to this series of problems. We have taken up the investigation of this problem again. The first communication on this subject follows below: it concerns the heats of combustion of a number of successive terms (C_2 — C_{13}) of the oxalic acid series.

We have chosen the series of normal saturated dicarboxylic acids for our first investigation for two reasons: in the first place this is one of the few homologous series in which all the terms necessary for our purpose, *both odd and even*, are relatively easy to obtain, and secondly Stohmann and his collaborators had already investigated this series up to and including sebacic acid and thereby noticed a most important phenomenon, namely, *the oscillation of the heat of*

¹⁾ Comp. H. Hartman, Dissertation Delft, 1925.

combustion-increments in successive terms of this series²⁾, regarding which we shall write in more detail later on in this paper (§ 5).

§ 2. *Apparatus and method; the heat capacity of the calorimetric system.*

While referring to some of our earlier publications attention need be drawn here only to a few points regarding the apparatus, the determination of the heat capacities and the method followed in the determinations of the heats of combustion.

The measurements published here extend over a period of several years and may be divided into two series. The first series contains by far the largest portion of the combustions of these dicarboxylic acids and was carried out in a platinum lined bomb of the construction devised by Langbein-Hugershoff, which was also used for all our earlier work. For the second series a Roth bomb was used of V₂A-steel, which we have found extremely satisfactory³⁾.

Details concerning the determination of the heat capacity (which amounted to about 2800 cal.₁₅^o) belonging to the first series of measurements, may be found in communications I and IV⁴⁾; it was determined by burning *benzoic acid*, the value of the heat of combustion of which was taken as 6324 cal.₁₅^o per gr. (air) (temp. 19° 5)⁵⁾ as accepted internationally. For the determination of the heat capacity belonging to the second series of measurements (which amounted to about 3050 cal.₁₅^o, mainly on account of the increase of the amount of water added to the system) *salicylic acid*, which has been proposed by us as the second thermochemical standard substance⁶⁾, was used along with benzoic acid; the heat of combustion of the former substance amounts to 5241.8 cal.₁₅^o per gr. (air)⁷⁾ (temp. 19° 5). The calibrations lying at the basis of the measurements with our Roth bomb are collected together in the following table in order to facilitate eventual criticism of our work.

²⁾ Compare e. g. Stohmann, Kleber, Langbein and Offenhauer, Verhandl. Sächs. Akad. Wiss. **45**, 605 (1893); J. prakt. Chem. (2) **49**, 117 (1894).

³⁾ See Verkade and Coops, Chem. Weekblad **21**, 282 (1924) (Comm. VII).

⁴⁾ I: Verkade, Coops and Hartman, Rec. trav. chim. **41**, 241 (1922); IV: Verkade and Coops, *ibid.* **42**, 205 (1923).

⁵⁾ Compare Verkade, *ibid.* **44**, 800 (1925).

⁶⁾ Verkade and Coops, Rec. trav. chim. **43**, 561 (1924) (Comm. VI).

⁷⁾ Recently Berner [J. Chem. Soc. **127**, 2747 (1925)] published the results of his determination of the heat of combustion of this acid, from which it should follow that the value given above is too high. We were able, however, to prove the correctness of our value in a recent research that will soon be published in the above mentioned journal.

Table 1.
Benzoic acid.

Weight of acid in grs. (air)	Correction for HNO ₃ , cotton, ignition and carbon	Final temperature	Observed rise in temperature	Correction for radiation etc.	Corrected rise in temp. x "Grad-wert"	Heat capacity in cal. 15°
0.76385	25.0 cal. 15°	21.15	1.5710	0.0060	1.5915	3050.9
0.75875	22.9	21.1	1.5595	0.0060	1.5795	3052.3
0.75315	21.0	21.05	1.5490	0.0045	1.5675	3051.8
0.77285	24.1	21.25	1.5865	0.0080	1.6090	3052.5
0.76945	26.7	21.1	1.5820	0.0060	1.6025	3053.0
0.75850	20.8	21.1	1.5590	0.0065	1.5795	3050.0
0.76285	21.7	21.05	1.5685	0.0065	1.5890	3049.6
0.76365	20.7	21.05	1.5700	0.0055	1.5895	3051.4
0.75200	26.1	21.05	1.5470	0.0065	1.5670	3051.6
0.76325	24.4	20.95	1.5700	0.0035	1.5880	3051.3
		Mean: 21.1				3051.4

Standard error of the arithmetic mean: 0.35 cal. = 0.1 per thousand }
 Maximum deviation from the arithmetic mean: 1.8 cal. = 0.6 per thousand }

Salicylic acid.

0.91970	26.7 cal. 15°	21.05	1.5710	0.0040	1.5890	3050.9
0.92000	22.0	21.05	1.5695	0.0050	1.5885	3049.8
0.91535	24.0	21.15	1.5610	0.0060	1.5810	3050.1
0.91645	24.3	21.05	1.5625	0.0050	1.5815	3053.0
		Mean: 21.1				3051.0

Standard error of the arithmetic mean: 0.70 cal. = 0.2 per thousand }
 Maximum deviation from the arithmetic mean: 2.0 cal. = 0.65 per thousand }

From these results we calculate for the heat capacity of the calorimetric system, containing the Roth bomb filled with oxygen up to a pressure of 35 atmos. and without the combustion products of either benzoic or salicylic acid, the value

$$3050.9 \pm 0.3 \text{ cal.}_{15^\circ} (\text{temp.} \pm 19^\circ.5).$$

With each substance examined the heat capacity of its combustion products was introduced in the usual way. *Therefore, the heats of combustion found hold for an isothermal reaction at the initial temperature of the measurements, which — with few exceptions (see below) — always amounted to $\pm 19^\circ.5$.*

Use has been made of the atomic weights corrected by Schoorl⁸⁾ for weighing in air, in calculating the molecular heats of combustion; the reduction to vacuum so obtained is sufficiently accurate for our purpose. The results of other investigators mentioned below have not been reduced to vacuum, since the corrections to be introduced into their data would almost always be within their experimental errors.

⁸⁾ Chem. Weekblad 15, 547 (1918); 22, 156 (1925).

At least two specimens of each substance were always burnt, which were either prepared by different methods or purified after concordant results were obtained on combustion, either by redistillation or by recrystallisation from another solvent than that used previously.

All melting points and boiling points mentioned were determined with the aid of calibrated shortened (Anschütz) thermometers.

The crystalline dicarboxylic acids were always carefully dried in a very finely powdered condition in a vacuum over phosphorus pentoxide.

In the tables given below each combustion is designated with a letter A—D indicating the method followed; these methods are described in detail in Communication VIII⁹⁾.

§ 3. The heats of combustion of a number of normal acids of the oxalic acid series.

Where we had to do with obtaining preparations of much greater purity than is usually attained, we have in some cases described in some detail the methods of preparation and purification followed. In the course of the thermochemical work we have in hand we have frequently come across difficulties because previous investigators were too sparing with such data.

1. Oxalic acid.

Pure commercial oxalic acid was recrystallised a few times from water and then dehydrated by introducing rather more than was necessary for a combustion into a weighing bottle and drying it by heating at 70°–80° to constant weight in a vacuum over phosphorus pentoxide. The acid while still warm was quickly pressed in a slightly warmed tablet press into loose pellets, which were then burnt with the addition of paraffin oil as auxilliary substance¹⁰⁾.

Table 2.
Oxalic acid.

No.	Method	Weight of acid in grs. (air)	Weight of auxil. subst. in grs. (air)	Total correction in cal. ¹⁵	Final temperature	Observed rise in temperature	Correction for radiation etc.	Corrected rise in temperature x "Gradwert"	Heat capacity in cal. ¹⁵	Heat of combustion per gram in cal. ¹⁵
1	D	0.96620	0.39700 p *)	4437.5	21.25	1.6470	0.0070	1.6690	3051.7	678.8
2	"	1.51650	0.33510 p	3750.7	21.15	1.5455	0.0070	1.5665	3051.8	679.1
3	"	1.57435	0.32960 p	3690.3	21.0	1.5410	0.0035	1.5585	3051.8	677.1
4	"	1.97320	0.31395 p	3517.1	21.0	1.5715	0.0045	1.5900	3051.9	676.9
Mean: 21.1										678.0

Standard error of the arithmetic mean: 0.6 cal. = 0.90 per thousand)

Maximum deviation from the arithmetic mean: 1.1 cal. = 1.60 per thousand)

*) p = paraffin oil.

⁹⁾ Verkade, Coops and Hartman, Rec. trav. chim. **44**, 206 (1925).

¹⁰⁾ For some details comp. Comm. VIII, loc. cit.

Notwithstanding, that in these measurements the sum of the corrections amounts to 70–85 % of the total heat evolution, the agreement of the results is very satisfactory. For the molecular heat of combustion at constant volume (Q_v) and at constant pressure (Q_p) we find the following mean values

$$Q_v = 61.0 \text{ Cal.}_{15^\circ} \quad Q_p = 60.1 \text{ Cal.}_{15^\circ}.$$

This value agrees completely with that of Stohmann, Kleber and Langbein¹¹⁾: 678.6 cal._{15°} per gr. (air) i. e. $Q_p = 60.2 \text{ Cal.}_{15^\circ}$. These investigators used "Kerzenstearinsäure", i. e. a mixture of palmitic and stearic acids as auxiliary substance in their oxalic acid combustions; at least 600 mgr. was necessary for a 2 gr. oxalic acid pastille. As a rule undesirably large quantities of carbon (in one case even 2.5 mgr.) remained behind in the combustion capsule, for which a correction had to be applied. The results of the individual measurements oscillate fairly considerably; the maximum deviation from the mean heat of combustion amounts to 5.5 parts per thousand as against only 1.6 parts in our measurements.

Further we meet with some *indirect* determinations of the heat of combustion of *anhydrous* oxalic acid in the literature, which may be given here for completeness.

Thomson¹²⁾ oxidised dilute aqueous oxalic acid solutions with a solution of hypochlorous acid and calculated that the quantity of heat evolved in the oxidation of dissolved oxalic acid by gaseous oxygen to gaseous carbon dioxide and water amounted to 62.0 Cal. He found –2.3 Cal. for the heat of solution of anhydrous oxalic acid, so that the heat of combustion of crystallised anhydrous oxalic acid should amount to $Q_p = 59.7 \text{ Cal.}$

Jahn¹³⁾ studied the electrolytic oxidation of aqueous potassium oxalate solutions in the ice calorimeter. From very excellent data, making use of the above mentioned heat of solution of anhydrous oxalic acid, he calculated the heat of combustion of this acid to be $Q_p = 60.5 \text{ Cal.}$ (maximum deviation from the mean 2 per thousand).

Luginin¹⁴⁾ derived the value $Q_p = 63.4 \text{ Cal.}$ for anhydrous oxalic acid from the heats of combustion of diethyl oxalate and ethyl alcohol and from data concerning the heat of esterification of oxalic acid; however, in a later communication¹⁵⁾ he takes without comment 60.0 Cal. as the heat of combustion of anhydrous oxalic acid. It can easily be shown that an error has crept in in the derivation of the first mentioned value.

2. Malonic acid.

A commercial sample of malonic acid was recrystallised from water at 50°–60° and combusted after drying (Nos. 5 and 6); it was then recrystallised from a mixture of acetone and ligroin and again combusted (Nos. 7 and 8).

Table 3.
Malonic acid.

5	D	1.70090	0.09330 p	1061.6	21.0	1.5685	0.0050	1.5880	2801.5	1991.4
6	..	1.71510	0.09105 p	1040.2	20.95	1.5685	0.0075	1.5900	..	1990.7
7	..	1.71200	0.09130 p	1042.8	21.0	1.5680	0.0070	1.5895	..	1992.0
8	..	1.66290	0.08920 p	1017.4	20.95	1.5260	0.0055	1.5450	..	1991.1

Mean: 21.0

1991.3

Standard error of the arithmetic mean: 0.3 cal. = 0.15 per thousand

Maximum deviation from the arithmetic mean: 0.6 cal. = 0.30 per thousand

¹¹⁾ J. prakt. Chem. (2) **40**, 202 (1889).

¹²⁾ Thermochem. Untersuch. II, 289 (1882).

¹³⁾ Ann. Phys. **37**, 435 (1889).

¹⁴⁾ Ann. chim. phys. (6) **8**, 140 (1886).

¹⁵⁾ Compt. rend. **107**, 597 (1888).

$$Q_v = 207.1 \text{ Cal.}_{15^\circ} \quad Q_p = 206.5 \text{ Cal.}_{15^\circ}.$$

Stohmann, Kleber and Langbein ¹¹⁾ found: $Q_p = 207.3 \text{ Cal.}_{15^\circ}$ (maximum deviation from the mean 1.6 ‰).

Luginin has burnt malonic acid twice; the first time he found Q_p to be 208.1 Cal. ¹⁴⁾ and afterwards ¹⁴⁾ 207.2 Cal. (max. deviation from the mean 5.7 ‰).

3. Succinic acid.

A commercial specimen of succinic acid was divided into two parts; one portion was recrystallised from a mixture of acetone and ligroin (Nos. 9 and 10) and the other was recrystallised from water and dried by warming to about 90° (Nos. 11 and 12).

Table 4.

Succinic acid.

9	C	1.43090	0.00970 n*	136.8	18.9 ¹⁷⁾	1.5790	0.0040	1.5935	2804.9	3028.0	}
10	"	1.42060	0.00955 n	141.3	18.5	1.5735	—	1.5840	"	3028.1	
11	B	1.40205	0.00410 n	73.2	20.2	1.5255	0.0035	1.5400	2804.3	3028.0	}
12	"	1.43240	0.00530 n	79.4	20.4	1.5595	0.0055	1.5765	"	2031.0	
mean: 19.5										3028.8	

Standard error of the arithmetic mean: 0.7 cal. = 0.25 per thousand /

Maximum deviation from the arithmetic mean: 2.2 cal. = 0.75 per thousand /

*) n = naphthalene.

$$Q_v = 357.4 \text{ Cal.}_{15^\circ} \quad Q_p = 357.1 \text{ Cal.}_{15^\circ}.$$

The agreement between the results obtained by methods C (combustion in powder form) and B (combustion in the form of a pellet) may be taken as quite satisfactory.

Stohmann, Kleber and Langbein ¹¹⁾ found $Q_p = 356.8 \text{ Cal.}_{15^\circ}$ (maximum deviation from the mean 1.1 ‰).

Luginin first found 355.8 Cal. ¹⁴⁾ and later ¹⁴⁾ 354.4 Cal. (maximum deviation from the mean 4.2 ‰).

4. Glutaric acid.

A specimen from Merck was purified by distillation in a vacuum (b. p. 185°/8 mms. with slight formation of anhydride) and then recrystallised first from toluene and subsequently from water (Nos. 13 and 14). The process of crystallisation was then repeated (Nos. 15 and 16). The acid melted at 98°.

¹⁴⁾ Ann. chim. phys. (6) 23, 179 (1891); as regards the trustworthiness of this investigators work see § 4.

¹⁷⁾ These and some subsequent measurements date from the beginning of our thermochemical work, when, unfortunately, sufficient attention was not given to the regulation of the temperature of the work room and the calorimeter water. The final temperature of the calorimeter water is therefore always lower and more variable than is now usual.

Table 5.
Glutaric acid.

13	B	1.10365	0.00830 n	107.5	21.05	1.5575	0.0035	1.5750	2800.5	3899.2
14	"	1.14700	0.00265 n	49.1	21.15	1.5970	0.0045	1.6160	"	3902.8
15	A	1.10550	—	28.9	21.1	1.5320	0.0035	1.5495	2801.3	3900.6
16	"	1.09620	—	29.8	21.1	1.5190	0.0045	1.5370	"	3900.6
Mean:					21.1					3900.8

Standard error of the arithmetic mean: 0.7 cal. = 0.20 per thousand }
 Maximum deviation from the arithmetic mean: 2.0 cal. = 0.50 per thousand }

$$Q_v = 514.9 \text{ Cal.}_{15^\circ} \quad Q_p = 514.9 \text{ Cal.}_{15^\circ}.$$

This value agrees excellently with one found by Stohmann and Kleber¹⁸⁾ for an acid recrystallised from water, ethyl acetate and acetone respectively, namely 515.0 Cal._{15°} (max. deviation from the mean 1.1 %₀₀). Some years previously Stohmann, Kleber and Langbein¹¹⁾ found a somewhat higher value: 517.2 Cal._{15°}. We obtained similar higher values, varying from 3905 to 3920 cal._{15°} per gram, for a specimen, which was crystallised only from boiling toluene and we consider that some anhydride is formed at the boiling point of this solvent (about 110°). The specimen used by Stohmann, Kleber and Langbein was however recrystallised from water so that there must be some other cause for the high heats of combustion found by these authors.

Massol¹⁹⁾ found the value $Q_p = 516.3$ Cal. for the heat of combustion of this acid: in our opinion these determinations are not to be relied on.

5. Adipic acid.

The adipic acid necessary for this investigation was prepared by oxidising cyclohexanol with nitric acid ($D = 1.2$)²⁰⁾. The adipic acid, which crystallised out from the reaction liquid on cooling, was filtered off, washed with cold water and recrystallised several times from water (No. 17); yield of acid recrystallised once from water 60 per cent. M. p. 153°. Another time the crude acid was first recrystallised several times from water, and then twice from a mixture of acetone and ligroin (Nos. 18 and 19).

Finally a beautiful specimen of adipic acid was placed at our disposal by Dr. van Loon (Nos. 20 and 21); this acid was also recrystallised again from water (No. 22).

The results of our heat of combustion determinations are collected together in the following table.

Table 6.
Adipic acid.

17	A	0.97990	—	22.9	20.4	1.5940	0.0025	1.6085	2804.1	4579.6
18	"	0.95055	—	29.6	20.2	1.5480	0.0035	1.5630	"	4579.7
19	"	0.94500	—	28.2	"	1.5400	0.0030	1.5545	"	4582.9
20	B	0.88130	0.00230 n	49.8	20.1	1.4420	0.0045	1.4575	"	4581.0
21	A	0.88340	—	25.0	20.1	1.4370	0.0035	1.4515	"	4579.2
22	"	0.94225	—	27.9	20.2	1.5305	0.0055	1.5475	"	4575.7
Mean:					20.2					4579.7

Standard error of the arithmetic mean: 1.0 cal. = 0.20 per thousand }
 Maximum deviation from the arithmetic mean: 4.0 cal. = 0.90 per thousand }

¹⁸⁾ J. prakt. Chem. (2) **45**, 475 (1892).

¹⁹⁾ See: Berthelot, Thermochimie II, p. 576 (1897).

²⁰⁾ Holleman, Slijper and van der Laan, Rec. trav. chim. **24**, 19 (1905).

$$Q_v = 668.6 \text{ Cal.}_{15^\circ} \quad Q_p = 668.9 \text{ Cal.}_{15^\circ}.$$

Stohmann, Kleber and Langbein ²¹⁾ found $Q_p = 668.9 \text{ Cal.}_{15^\circ}$ (max. deviation from the mean $1.8 \text{ }^{\circ}/_{100}$) for a specimen melting at 150.6° prepared according to Wislicenus ²¹⁾ by heating β -iodopropionic acid with molecular silver.

6. Pimelic acid.

We tried at first to obtain pimelic acid by the method of Lumsden and Walker ²²⁾, namely by the reduction of amyl salicylate with sodium and boiling amyl alcohol. We were not satisfied with this method of preparation however, the yield being very small ²³⁾.

Good results were obtained however by the synthesis described by von Braun ²⁴⁾. When N-benzoylpiperidine is heated with phosphorus pentabromide an equimolecular mixture of 1:5-dibromopentane and benzonitrile is obtained. The crude 1:5-dibromopentane is then converted into 1:5-dicyanopentane by heating with potassium cyanide in alcoholic solution and this hydrolysed to pimelic acid.

N-Benzoylpiperidine, obtained by benzoylating piperidine ²⁵⁾ was purified by distillation in a vacuum; the boiling point was 172° — 173° at 9 mms., the melting point 48° and the yield 90 per cent.

One hundred grams of this substance were heated in a distillation flask with 228 gr. phosphorus pentabromide until the whole mass became liquid, after which the contents of the flask were kept at this temperature for half an hour and then fractionated at 12 mms.; at first phosphorus oxybromide passed over and then a mixture of 1:5-dibromopentane and benzonitrile (between 70° and 110°), while a tarry residue remained behind. Ice water was added to the whole of the distillate in order to decompose the oxybromide, and then dibromopentane and benzonitrile were separated from the liquid by means of a current of steam; a part of the benzonitrile was hydrolysed during this operation to benzoic acid. Dibromopentane and the resulting benzonitrile were isolated together from the distillate in the usual way (yield 150 gr.).

To 75 gr. of the mixture of these two substances were added a cold saturated aqueous solution of 40 gr. potassium cyanide and enough absolute alcohol to keep the potassium cyanide and the two organic substances in solution. The solution was then boiled under a reflux condenser. The conversion into 1:5-dicyanopentane takes place very slowly. After boiling for 40 hours the alcohol was distilled off and steam passed through the brown coloured mass remaining behind to remove benzonitrile and unchanged dibromopentane ²⁶⁾, while dicyanopentane

²¹⁾ Ann. **149**, 220 (1869).

²²⁾ J. Chem. Soc. **79**, 1198 (1901); Einhorn and Lumsden, Ann. **286**, 259 (1895).

²³⁾ Also Voerman (Diss. Groningen 1903, p. 43) was unable to obtain satisfactory results by using this method.

²⁴⁾ Ber. **37**, 3588 (1904).

²⁵⁾ Schotten, *ibid.* **17**, 2545 (1884); **21**, 2238 (1888).

²⁶⁾ This mixture can be worked up again for dinitrile, e. g. together with a new portion of dibromopentane and benzonitrile.

remained behind. The latter was taken up in ether and after washing and drying, the ethereal solution was distilled in a vacuum; b. p. of 1 : 5-dicyanopentane 171° — 172° /12 mms. The total yield from 100 gr. N-benzoylpiperidine was 30 gr. or 47% of theory.

The dinitrile is easily hydrolysed by boiling for half an hour with 15 parts of 60% sulphuric acid. After the substance had dissolved the dark coloured solution was diluted with an equal volume of water, the partially precipitated pimelic acid taken up in ether, and after removal of the solvent, recrystallised successively from water, twice from acetone and finally from toluene. This preparation (m. p. 105°) was used for combustions Nos. 23 and 24.

Combustions Nos. 25, 26 and 27 were carried out on a specimen of pimelic acid, which was obtained from *ethyl pentane-1 : 1 : 5 : 5-tetracarboxylate* on boiling with hydrochloric acid²⁷⁾.

A solution of 46 gr. sodium (2 atoms) in 500 gr. absolute alcohol was added slowly to a mixture of 202 gr. (1 mol.) trimethylene bromide and 640 gr. (4 mols.) ethyl malonate. After warming on the water bath for three hours the reaction was neutral. Water was now added and the excess of ethyl malonate distilled off in a current of steam. The oil remaining behind was extracted with ether, the latter distilled off and the residue fractionated in vacuo. The fraction boiling at 185° — 230° /10 mms. (for the greater part at 200° — 210°) was collected separately; it consisted of crude ethyl pentane-1 : 1 : 5 : 5-tetracarboxylate, the yield being 50% of the theory.

This ester was boiled under a reflux condenser with two volumes of 20 per cent. hydrochloric acid until all the ester had disappeared, which took about 18 hours. The solution was then evaporated to dryness and the pimelic acid remaining behind distilled in a vacuum; b. p. 210° — 215° at 17 mms. By crystallisation first from water then twice from acetone and finally from toluene the acid was obtained quite pure; m. p. 105° — $105^{\circ}.5$.

Table 7.
Pimelic acid.

23	A	0.82575	—	30.0	21.05	1.5175	0.0045	1.5355	2800.4	5171.2	}
24	B	0.81430	0.00790 n	111.3	21.1	1.5240	0.0055	1.5435	..	5171.5	
25	A	0.82455	—	22.8	21.25	1.5100	0.0060	1.5295	2800.7	5167.5	}
26	..	0.81735	—	21.2	21.30	1.4945	0.0085	1.5165	..	5170.5	
27	..	0.82550	—	21.9	21.30	1.5130	0.0040	1.5305	2801.2	5166.9	}
					Mean: 21.20						5169.5

Standard error of the arithmetic mean: 1.0 cal. = 0.20 per thousand }

Maximum deviation from the arithmetic mean: 2.6 cal. = 0.50 per thousand }

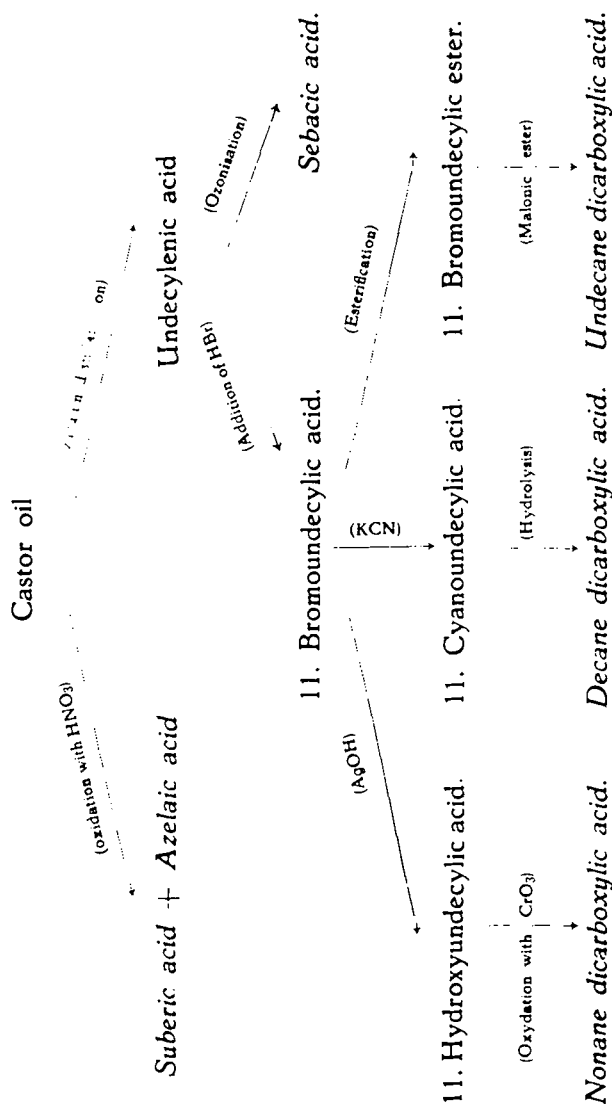
$$Q_v = 827.1 \text{ Cal.}_{15^{\circ}}$$

$$Q_p = 827.7 \text{ Cal.}_{15^{\circ}}$$

²⁷⁾ Perkin jun., Ber. 18, 3248 (1885); J. Chem. Soc. 51, 241 (1887); Perkin jun. and Prentice, ibid 59, 823 (1891) — von Baeyer, Ann. 278, 100 (1894).

Stohmann and Kleber¹⁸⁾ found the value 828.9 Cal.₁₅[°] (max. deviation from the mean 0.4%) for the heat of combustion at constant pressure; their acid, melting at 103°, was prepared by Perkin's method. Stohmann, Kleber and Langbein¹¹⁾ had previously found 829.6 Cal.₁₅[°] for a product obtained by the oxidation of cyclopentanone; this last value is certainly less reliable.

The dicarboxylic acids with 8–13 carbon atoms were all obtained in some way or other starting from *castor oil*. The following scheme gives a diagrammatic representation of the methods of preparation followed, which will be discussed in more detail later on where necessary.



7. *Suberic acid.*

Castor oil was saponified by boiling with alcoholic potash; 120 gr. potassium hydroxide in a litre of 96% alcohol was added to 500 gr. oil. Most of the alcohol was then distilled off, the fatty acids liberated with dilute hydrochloric acid, washed with water and dried on the water bath in a current of dry air. In all 11500 gr. of fatty acids were worked up.

Quantities of 500 gr. of this crude ricinoleic acid were heated on a sand bath in a 5 litre flask into which nitric acid ($D = 1.36$) was carefully run. The oxidation took place with very violent frothing. After 1500 gr. nitric acid had been added in the course of about 3 hours, the mixture was boiled for a day. Water was then added and the considerable quantities of crude heptylic acid, which are formed in the oxidation removed in a current of steam. After the steam distillation there are present in the flask not inconsiderable quantities of oil besides the aqueous solution. This oil was separated off, extracted repeatedly with hot water, then again oxidised in the same way (the reaction is not so violent now) and treated as described above; the oil, which separated this time, about 60 gr., was rejected.

The two aqueous solutions together with the water used in the extraction of the oils were then evaporated down until they formed a thick mass of crystals on cooling. This crystalline mass was well filtered, washed with water and recrystallised once from water. We obtained about 1800 gr. altogether of this mixture of *suberic* and *azelaic acids*: it consisted of about 60% of *suberic* and 40% of *azelaic acid*.

In order to separate these two acids in a pure condition from this mixture we have made use of the method published some time ago by Day, Kon and Stevenson²⁸⁾ combined with a fractional crystallisation of the magnesium salts²⁹⁾.

According to the first mentioned paper, 300 gr. of the dry mixture of acids were suspended in 1500 ccs. boiling benzene and absolute alcohol was then added until everything just passed into solution; about 300 ccs. was necessary for the acid mixture we obtained. *Suberic acid* slowly separated on cooling the filtered solution. This was filtered off and washed with cold benzene. Already it appeared to be fairly pure; it sintered from about 134° and melted at 137°--140°. The total yield of this acid was 640 gr.

For further purification the *suberic acid* was very finely powdered and extracted with three times its weight of dry ether at room temperature to remove any *azelaic acid*, which might be present. The portion insoluble in ether was filtered off and then crystallised three times from water. It was then used for combustions Nos. 28 and 29.

²⁸⁾ J. Chem. Soc. 117, 641 (1920).

²⁹⁾ See for example: Ettaix, Ann. chim. phys. (7) 9, 381 (1896).

This preparation was recrystallised from acetone and then from water and again burnt (Nos. 30 and 31); m. p. 141°.

Reference must be made to the next section of this § for details of the working up of the benzene alcoholic mother liquor for azelaic acid; appreciable quantities of *suberic acid* may be recovered from the mixture of acids remaining after the separation of azelaic acid.

Table 8.
Suberic acid.

28	C	0.75385	0.01080 n	138.7	21.15	1.5515	0.0040	1.5695	2801.0	5647.7 }
29	"	0.75000	0.00610 n	96.3	21.1	1.5245	0.0080	1.5460	"	5645.4 }
30	B	0.75000	0.00660 n	97.7	21.1	1.5300	0.0030	1.5465	2800.4	5644.2 }
31	"	0.74650	0.00630 n	97.0	21.2	1.5200	0.0060	1.5395	"	5645.3 }
Mean:					21.15	5645.7				

Standard error of the arithmetic mean: 0.7 cal. = 0.15 per thousand (

Maximum deviation from the arithmetic mean: 2.0 cal. = 0.35 per thousand (

$$Q_v = 982.4 \text{ Cal.}_{15^\circ}$$

$$Q_p = 983.2 \text{ Cal.}_{15^\circ}.$$

Stohmann, Kleber and Langbein¹¹⁾ found the value 985.6 Cal._{15°} for the heat of combustion at constant pressure. However, Stohmann and Kleber¹⁸⁾ considered it possible that this specimen still contained some azelaic acid. They therefore distilled it in vacuo and recrystallised the distillate several times from ether, then from water and combusted it afresh; they then obtained the value 953.7 Cal._{15°} (max. deviation from the mean 0.5 %₁₀₀).

Luginin first found 993.2 Cal.¹⁹⁾ for a specimen prepared from cork, and later¹⁶⁾ 989.5 Cal. (max. deviation from the mean 3.2 %₁₀₀).

8. *Azelaic acid.*

The solvent was completely removed from the above mentioned benzene-alcoholic mother liquor. The mixture of acids remaining behind was introduced into a large quantity of boiling water and converted into the magnesium salts with an excess of magnesium carbonate. The filtered solution was evaporated down to incipient crystallisation and the magnesium azelate, which crystallised out on cooling was filtered and washed thoroughly with as little water as possible. The filtrate and washings were then combined and again evaporated down to incipient crystallisation and a second fraction obtained. After being recrystallised from water if necessary, these two fractions gave practically pure *azelaic acid* on acidification, sintering from 103° and melting at 105°—107°. In all 470 grams were obtained.

In order to purify the acid further, it was crystallised first from water, then from a mixture of acetone and ligroin (Nos. 32 and 33). Another specimen was recrystallised several times from water³⁰⁾ (Nos. 34 and 35); m. p. 107°—108°.

³⁰⁾ It was afterwards observed that this acid and also suberic acid can be purified quite satisfactorily by esterification in methyl alcoholic hydrochloric acid and careful fractionation of the dimethyl esters in a vacuum (see communication XIII).

Table 9.
Azelaic acid.

32	A	0.73705	--	32.8	$\overset{\circ}{20.1}$	$\overset{\circ}{1.5905}$	$\overset{\circ}{0.0035}$	$\overset{\circ}{1.6060}$	2804.1	6065.5
33	"	0.72530	—	31.8	20.1	1.5655	0.0030	1.5805	"	6066.6
34	"	0.73375	—	25.2	20.2	1.5710	0.0065	1.5965	"	6066.8
35	"	0.73605	—	27.5	$\overset{\circ}{20.1}$	1.5835	0.0075	1.6025	"	6067.7
Mean:					$\overset{\circ}{20.1}$	6066.7				

Standard error of the arithmetic mean: 0.3 cal. = 0.05 per thousand }

Maximum deviation from the arithmetic mean: 1.2 cal. = 0.20 per thousand }

$$Q_v = 1140.4 \text{ Cal.}_{15^\circ}$$

$$Q_p = 1141.7 \text{ Cal.}_{15^\circ}$$

For the value of the heat of combustion of this acid at constant pressure, Stohmann, Kleber and Langbein³¹⁾ found 1141.3 Cal._{15°} (max. deviation from the mean 0.9 %).

Hydrochloric acid was added to the mother liquor remaining over from the recovery of magnesium azelate; the precipitated acids were well filtered, washed with water and carefully dried. The treatment described above can now be repeated with this mixture of acids; on crystallisation from a mixture of benzene and absolute alcohol, suberic acid is obtained and subsequent fractionation of the magnesium salts gives azelaic acid. The mother liquor obtained from this batch of magnesium salts can be worked up again in the same way³¹⁾.

In this way, from about 1800 grs. crude acids, produced by the oxidation of 11.5 kilos. crude ricinoleic acid with nitric acid, we obtained:

1025 gr. *suberic acid* = 8.9 % of the weight of ricinoleic acid taken.

555 gr. *azelaic acid* = 4.8 % " " " " " " " "

In a separate publication one of us (V.) will discuss certain points which have come forward during the above described preparation of these acids.

9. Sebacic acid.

Combustion No. 36 was carried out with a preparation obtained by careful distillation of the sodium soap from ricinoleic acid with very concentrated caustic soda solution³²⁾. The crude sebacic acid obtained by acidifying the residue from the distillation was purified by crystallisation several times from water and finally from a mixture of acetone and petroleum ether.

For the other combustions sebacic acid was prepared by the ozonisation of undecylenic acid. For this preparation the method

³¹⁾ A mixture of suberic and azelaic acids of the composition obtained by us, may also be worked up by the method published by Miss Carmichael: J. Chem. Soc. 121, 2545 (1922). In this case, however, very large quantities of ether are used in the separation and the losses may be somewhat larger.

³²⁾ Bödtker, Diss. Leipzig, 1891, p. 2; Ber. 39, 2765 (1906) note. — For the method of heating the castor soap with alkali compare in particular Roger Adams c. s., Organic Synthesis I, 61 (1921) and further Freund and Schönfeld, Ber. 24, 3352 (1891).

given by Miss Noorduyn³³⁾ was followed with practically no modifications. The ozonide peroxide obtained was decomposed by boiling for two hours under a reflux with 16 times its weight of water. Steam was then passed through the liquid for some time in order to remove volatile decomposition products (formic acid; formaldehyde?). It was then made weakly alkaline and the 9-nonanone-1-carboxylic acid, which is present along with sebacic acid was oxidised with a dilute potassium permanganate solution, ice being added to keep the liquid cool. After the manganese dioxide, which was precipitated had been filtered off and carefully washed, the liquid was acidified, when practically pure sebacic acid (m. p. 130°—131°), was precipitated. The yield of acid after crystallising from water was 60%; m. p. 133°.

This acid was still crystallised from toluene and water and then used for combustions Nos. 37 and 38. Combustions Nos. 39 and 40 were made after the acid had again been recrystallised from water.

Table 10.
Sebacic acid.

36	A	0.66705	—	40.7	20.1	1.5240	0.0050	1.5405	2804.1	6414.9
37	..	0.67360	—	31.9	21.0	1.5350	0.0055	1.5545	2401.2	6417.0
38	..	0.67785	—	32.8	21.2	1.5450	0.0050	1.5640	..	6414.8
39	C	0.68495	—	37.3	20.95	1.5610	0.0065	1.5815	2801.8	6414.6
40	..	0.67710	—	33.3	21.05	1.5420	0.0060	1.5620	..	6414.3
				Mean:	20.85					
									6415.2	

Standard error of the arithmetic mean: 0.6 cal. = 0.10 per thousand)

Maximum deviation from the arithmetic mean: 1.8 cal. = 0.30 per thousand)

$$Q_v = 1295.9 \text{ Cal.}_{15^\circ} \quad Q_p = 1297.3 \text{ Cal.}_{15^\circ}$$

Stohmann, Kleber and Langbein¹¹⁾ found for Q_p the value 1297.1 Cal._{15°} (max. deviation from the mean 0.7 %₀₀) and Luginin first 1297.1 Cal._{15°} and later 1293.4 Cal._{15°} (max. deviation from the mean 3.3 %₀₀).

10. *Nonane dicarboxylic acid.*

This acid was also prepared starting from undecylenic acid; from this 11-bromoundecylenic acid was obtained according to the directions of Walker and Lumsden³⁴⁾:

Undecylenic acid (25 gr.) was dissolved in 20 gr. dry toluene and saturated at 0° with bromine free hydrogen bromide, dried by means of phosphorus pentoxide. 11-Bromoundecylenic acid soon separated; the cooled mass was filtered and the acid recrystallised from petroleum ether; yield 50—65 %₀. M. p. 57°.

Starting from 11-bromoundecylenic acid, 11-hydroxyundecylenic acid was obtained as follows³⁴⁾:

The bromo-acid (53 gr.), dissolved in 200 ccs. N-sodium hydroxide was warmed to 60°—70° for 24 hours with an excess of freshly

³³⁾ Rec. trav. chim. **38**, 326 (1919). — See also Grün and Wirth, Ber. **55**, 2205 (1922) for some details regarding the ozonisation of ethyl undecylenate.

³⁴⁾ J. Chem. Soc. **79**, 1191 (1901).

precipitated silver hydroxide (obtained from 110 gr. silver nitrate) with constant stirring. The liquid was then filtered and the filtrate acidified with dilute nitric acid. The hydroxy acid, which was precipitated, was filtered off, dried and recrystallised from benzene. Yield 80%; m. p. 70°.

The oxidation of the hydroxy acid to *nonane dicarboxylic acid* was achieved with chromic acid in acetic acid solution³⁴); 1 gr. chromic oxide in 10 ccs. glacial acetic acid being added for each gram of hydroxy acid. After standing at room temperature for 24 hours the mixture was warmed for some time on the water bath. On diluting the resulting reaction product with water nonane dicarboxylic acid was precipitated. In order to obtain the acid quite free from chromium derivatives, it was filtered, dissolved in potassium hydroxide solution, the solution boiled for some time and filtered hot. The dicarboxylic acid precipitated on acidifying the filtrate melted at 110°; yield about 70%.

Three separate preparations were used in the combustions namely, No. 41, recrystallised from acetone, benzene and water, No. 42, crystallised twice from water and Nos. 43 and 44 recrystallised from water and dilute alcohol.

Table 11.

Nonane dicarboxylic acid.

41	A	0.64020	..	15.9	21.15	1.5290	0.0050	1.5480	2800.7	6731.6
42	..	0.65190	..	29.6	21.1	1.5570	0.0055	1.5765	2801.2	6728.8
43	D	0.55165	0.10485 p	1198.6	21.05	1.5925	0.0035	1.6100	3051.6	6733.5
44	..	0.55735	0.09215 p	1055.7	21.1	1.5560	0.0050	1.5750	..	6729.3
					Mean: 21.1					
										6730.8

Standard error of the arithmetic mean: 0.9 cal. = 0.15 per thousand

Maximum deviation from the arithmetic mean: 2.7 cal. = 0.40 per thousand

$$Q_v = 1453.8 \text{ Cal.}_{15^\circ} \quad Q_p = 1455.6 \text{ Cal.}_{15^\circ}$$

11. Decane dicarboxylic acid.

This acid was prepared from 11-bromoundecylic acid by the method given by Walker and Lumsden³⁵). The bromo-acid was dissolved in caustic soda and boiled for 20 hours with an excess of potassium cyanide, after which the solution was saturated with gaseous hydrochloric acid and boiled to convert the *11-cyano-acid* first formed into decane dicarboxylic acid. After one crystallisation from water it melted at 126°.5, the yield being 40%.

Two similar preparations were each recrystallised once from dilute alcohol and burnt (Nos. 45 and 46, and 47 and 48 respectively); one of the preparations was then crystallised from a mixture of acetone and ligroin and again burnt (No. 49).

³⁴) J. Chem. Soc. 79, 1197 (1901). — Compare Noerdlinger, Ber. 23, 2356 (1890).

Table 12.

Decane dicarboxylic acid.

45	A	0.71880	—	38.1	21.0	1.6415	0.0040	1.6605	3051.6	6996.5
46	"	0.70990	—	40.5	21.1	1.6215	0.0040	1.6405	"	6994.8
47	"	0.67810	—	38.9	21.05	1.5485	0.0040	1.5665	"	6992.2
48	"	0.66135	—	39.5	20.95	1.5125	0.0025	1.5285	"	6993.1
49	"	0.67450	—	38.8	21.0	1.5410	0.0035	1.5585	"	6993.5
				Mean:	21.0					6994.0

Standard error of the arithmetic mean: 0.8 cal. = 0.10 per thousand }

Maximum deviation from the arithmetic mean: 2.5 cal. = 0.35 per thousand }

$$Q_v = 1608.2 \text{ Cal.}_{15^\circ}$$

$$Q_p = 1610.7 \text{ Cal.}_{15^\circ}$$

12. Undecane dicarboxylic acid (*Brassylic acid*).

Two methods were adopted for the preparation of brassylic acid. First of all, following exactly the procedure laid down by Lumsden and Walker ³⁶), ethyl 11-bromo-undecylate (b. p. 169°—170°/7 mms.) was condensed with ethyl sodiomalonate. After boiling for 36 hours on the water bath the liquid reacted neutral. The reaction product was isolated in the usual way and without further purification hydrolysed with alcoholic potash and the 1:1:11-undecane tricarboxylic acid so formed isolated and dried. On heating to 120° carbon dioxide was evolved and the brassylic acid remaining behind was recrystallised first from water and then from dilute alcohol (Nos. 50 and 51). M. p. 112°—113°; yield 15 %.

Afterwards brassylic acid was obtained by the ozonisation of erucic acid. This ozonisation was carried out exactly like that of oleic acid, which has often been described in the literature ³⁷).

Erucic acid (5 gr.) was dissolved in 100 ccs. dry chloroform and ozonised at 5°—10° (ozone content of oxygen about 10 %; velocity of gas stream about 7½ litres per hour). After 3 hours had elapsed the liquid became blue in colour. The chloroform was then distilled off in a vacuum and the resulting ozonide peroxide was split up by boiling it under a reflux with four times its weight of water. The supernatant oil, which became solid on cooling, was taken up with ether and the ethereal solution shaken with sodium bicarbonate solution; in this way all the brassylic acid and most of the 12-dodecanone-1-carboxylic acid (brassylic monoaldehydic acid) passed into the aqueous layer as sodium salt, while nonylic aldehyde, nonylic acid and the remainder of the brassylic monoaldehydic acid remained behind in the ether ³⁸). The aqueous solution of the sodium salts was acidified with sulphuric acid and the precipitate taken up in ether. After evaporating the solvent 2.5 gr. of a white substance remained melting at 90°—93°.

³⁶) J. Chem. Soc. 79, 1191 (1901). — Compare Krafft and Saldis, Ber. 33, 3571, 3574 (1900); Komppa, ibid. 34, 898 (1901).

³⁷) Compare for example Harries and Thieme, Ann. 343, 357 (1905); Ber. 39, 2844 (1906); Harries and Türk, ibid. 39, 3732 (1906); Frank, Ann. 374, 356 (1910).

³⁸) The ethereal solution can be worked up for these three constituents in the usual way by fractional distillation; this, however, is of no importance for our purpose.

which was a mixture of brassylic acid and its semi-aldehyde. This mixture was dissolved in soda solution, cooled in ice and oxidised completely to brassylic acid with dilute potassium permanganate. The brassylic acid so obtained was crystallised first from water and then twice from dilute alcohol. (Nos. 52 and 53); m. p. 113°.

Table 13.

Brassylic acid.

50	D	0.52750	0.09535 p	1093.1	21.2	1.5875	0.0080	1.6100	3051.6	7241.7
51	..	0.44065	0.12380 p	1409.9	21.0	1.4915	0.0025	1.5075	..	7240.2
53	A	0.67715	—	39.3	21.15	1.5995	0.0045	1.6185	..	7235.8
54	..	0.67820	—	37.8	21.05	1.6025	0.0045	1.6210	..	7238.0
Mean:					21.1	7238.9				

Standard error of the arithmetic mean: 1.3 cal. = 0.20 per thousand }

Maximum deviation from the arithmetic mean: 3.1 cal. = 0.45 per thousand }

$$Q_v = 1766.3 \text{ Cal.}_{15^\circ} \quad Q_p = 1768.6 \text{ Cal.}_{15^\circ}.$$

§ 4. Summary of the heats of combustion.

The molecular heats of combustion at constant pressure, which we have found, (which hold for an isothermal reaction at 19°·5) are given in Table 14. There too are given the results obtained by Stohmann, Kleber and Langbein or those of Stohmann and Kleber if the latter have repeated the measurements of the authors first mentioned (as is the case with glutaric acid, pimelic acid and suberic acid); the fourth column contains the results obtained by Luginin during his second investigation (1891), the only one concerning which details are published and from which we can judge therefore to some extent as to its accuracy.

Table 14.

		<i>Stohmann etc.</i>	<i>Luginin</i>
Oxalic acid	60.1 Cal. _{15°}	60.2 Cal. _{15°}	—
Malonic acid	206.5	207.3	207.2 Cal. +0.3 % ₁₀
Succinic acid	357.1	356.8	354.4 —0.8 % ₁₀
Glutaric acid	514.9	515.0	—
Adipic acid	668.9	668.9	—
Pimelic acid	827.7	828.9	—
Suberic acid	983.2	983.7	989.5 +0.6 % ₁₀
Azelaic acid	1141.7	1141.3	—
Sebacic acid	1297.3	1297.1	1293.4 —0.3 % ₁₀
Nonane dicarboxylic acid	1455.6	—	—
Decane dicarboxylic acid	1610.7	—	—
Brassylic acid	1768.6	—	—

The agreement between our results and those of Stohmann and his co-workers is always very good, which is all the more remarkable since the latter investigators often burnt only one specimen of each acid and so they generally missed the security, which is given by a fresh combustion of a specimen after recrystallisation or redistillation. The small differences between Stohmann's results and our own will appear to be of very great importance presently. In

connection with certain work we shall publish later it is of importance to point out that all these measurements of Stohmann and his collaborators were made before the recalibration of their apparatus in 1893³⁹⁾.

On the other hand the results of Luginin deviate considerably. The deviations from the values we have found, given in the last column of table 14 are both positive and negative and therefore are certainly not to be put down only to an incorrect determination of the heat capacity of the calorimetric system by the investigator mentioned or to an uncertainty in the heat unit used. The work of this investigator certainly cannot claim great accuracy; this is obvious for example from the large variation in the heats of combustion obtained when burning one and the same preparation (compare the max. deviation from the mean heat of combustion which is always given in the previous §) and from the fact that the mean heats of combustion found for two specimens of the same substance very often lie considerably apart.

§ 5. *Heat of combustion and homology.*

In the sequel in order to indicate the position of a compound in a homologous series we shall introduce the conception of "term number", to some extent analogous to the well known conception "atomic number". The successive terms of a series are numbered in such a way that the term with the smallest number of carbon atoms is indicated by the number 1, the succeeding term by the number 2 and so on. An even term is then a term with an even term number. It must be kept in mind that an even term in the series of dicarboxylic acids considered here contains an odd number of carbon atoms, while on the other hand, in the fatty acid series, for example, it contains an even number of carbon atoms.

It is clearly evident from Table 15 that in the homologous series of normal saturated dicarboxylic acids we can in no wise speak of a constant increase in the heat of combustion as we ascend the series. Leaving oxalic and malonic acids out of the question for the moment (compare § 6) we at once see how large and small *increments in the heat of combustion*, Δ_{CH_2} , regularly follow one another; the increments amount alternately to about 158 and about 155 Cal._{15°}. The largest increment is obtained in introducing a methylene group into an acid with an odd term number, i. e. with an even number of carbon atoms. However if we consider the acids with even and those with odd term numbers as belonging to two different homologous series, we find increments in the heat of combustion ($\Delta_{C_2H_4}$) which fluctuate but slightly in both these series.

In the normal saturated dicarboxylic acids, therefore, we can distinguish two thermal homologous series, containing respectively the acids with even term numbers and the acids with odd term numbers.

³⁹⁾ Stohmann, Kleber, Langbein and Offenhauer, Ber. Verh. sächs. Ges. Wiss. **45**, 605 (1893).

Table 15.

Term number		Q_p	Δ_{CH_2}	$\Delta_{C_2H_4}$
1	C_2	60.1 Cal. _{15°}		
			146.4	
2	C_3	206.5		
			150.6	
3	C_4	357.1		
			157.8	
4	C_5	514.9		311.8
			154.0	
5	C_6	668.9		
			158.8	
6	C_7	827.7		314.3
			155.5	
7	C_8	983.2		
			158.5	
8	C_9	1141.7		314.1
			155.6	
9	C_{10}	1297.3		
			158.3	
10	C_{11}	1455.6		313.4
			155.1	
11	C_{12}	1610.7		
			157.9	
12	C_{13}	1768.6		

This phenomenon of the oscillation of increments in the heat of combustion could be deduced already from the results obtained by Stohmann and his collaborators (compare table 14) and was in fact already noticed by these investigators⁴⁰⁾. However, in our experiments the phenomenon comes more to the front. On the one hand, because the series of acids investigated was extended by three more terms; on the other hand and especially because both the two alternating increments in the heats of combustion appeared to fluctuate so very slightly — which is not yet apparent from Stohmann's data — the mean values for these two increments amounting to:

odd \rightarrow even term number: $\Delta_{CH_2} = 158.3 \pm 0.2$ Cal._{15°}

even \rightarrow odd term number: $\Delta_{CH_2} = 155.1 \pm 0.4$ Cal._{15°}.

As a matter of fact these fluctuations are so small that the possibility arises that they should be ascribed solely to errors of observation in the determinations of the heats of combustion. This would indicate that in each of the two thermal homologous series, which together make up the series of normal, saturated dicarboxylic acids, the heat of combustion should be a *purely additive quantity*.

⁴⁰⁾ Compare Stohmann, Kleber and Langbein, J. prakt. Chem. (2) **40**, 220 (1889); Stohmann, Kleber, Langbein and Offenbauer, ibid. (2) **49**, 117 (1894) and Ber. Verh. Sächs. Ges. Wiss. **45**, 605 (1893).

In our preliminary communication on the heats of combustion of successive terms of homologous series⁴¹⁾ we still made a strong reservation on this point. However, closer investigation of various other homologous series — to be published later — has shown us that, although in general the molecular heat of combustion besides being of an additive nature is also certainly strongly influenced by structural considerations, *the additive character is very predominant in the higher terms of these homologous series*, so that between the successive higher terms of the thermal homologous series increments in the heat of combustion are found, which are constant within the experimental error.

We cannot pass on without mentioning that already many years ago, it was particularly Stohmann who tried to make it clear, from a huge mass of data, that in a *thermal* homologous series at least with the higher terms, the heat of combustion is an additive quantity, i. e. that actually constant increments in the heat of combustion occur between successive terms of this series. This proof however has never been conclusive, for several reasons which need not be mentioned here⁴²⁾; the fluctuations in the successive increments were generally not inconsiderable and at any rate not negligible.

Moreover, the same thing has been noticed for various physical properties such as, for example, molecular refraction and magnetic molecular rotation by numerous investigators and from an enormous amount of material.

Finally if we calculate the mean increment in the heat of combustion for the group $-\text{CH}_2-\text{CH}_2-$ (represented by $\Delta_{\text{C}_2\text{H}_4}$) for the odd and even terms, starting from succinic and glutaric acids respectively as the first terms of these two series and making use of all the results in the same way as is done e. g. by Eykman⁴³⁾ for the molecular refraction, we find

$$\begin{array}{ll} \text{Odd series (1st term succinic acid) } 10 \Delta_{\text{C}_2\text{H}_4} = 3131.7 \\ \Delta_{\text{C}_2\text{H}_4} = 313.2 \text{ Cal.}_{15^\circ} \\ \text{Even series (1st term glutaric acid) } 10 \Delta_{\text{C}_2\text{H}_4} = 3134.0 \\ \Delta_{\text{C}_2\text{H}_4} = 313.4 \text{ Cal.}_{15^\circ}. \end{array}$$

The greatest deviation from these mean values amounts in both series to only 0.5 % and 0.2 % respectively.

In how far we may speak here of the complete additive character of the heat of combustion will only be evident from a still closer investigation after previous refinement of the methods of measurement.

In the first place one may ask whether an oscillation in the increments Δ_{CH_2} occurs in other homologous series and if so, in which homologous series, for which form of aggregation of the

⁴¹⁾ Verslag. Akad. Wetenschappen Amsterdam 33, 766 (1924).

⁴²⁾ Of course we shall deal with this question each time we study a homologous series, which has already been the object of Stohmann's investigations.

⁴³⁾ Rec. trav. chim. 12, 157 (1893) and others.

terms investigated, in what way (alternation of two increments each fluctuating but slightly or of two increments which alter gradually) and in what degree. An extensive amount of material for answering these questions has already been collected by the authors, while several other homologous series are either being examined or are on their program.

Secondly we have submitted the literature on the oscillation of various other physical and physicochemical constants of successive terms of different homologous series to a careful critical investigation and also with the help of data recorded in the literature we have ourselves inaugurated an extensive investigation of these oscillation phenomena.

Combining these two branches of our study has finally put us in a position to survey the problem of the course of the molecular heat of combustion in successive terms of homologous series in its general aspect. We hope to develop gradually our ideas concerning this matter in subsequent communications.

§ 6. *The heats of combustion of the initial terms of this homologous series.*

We see quite clearly from table 15 that *oxalic acid and malonic acid take up an exceptional position in the series before us*. The differences in molecular heat of combustion between these two acids themselves and between the latter acid and succinic acid are considerably smaller than that found between two other, arbitrarily chosen, successive terms of this homologous series. These abnormal increments in the heat of combustion obviously find their cause in the fact *that these two initial terms have an abnormally large energy content*.

In opposition to what we found with the higher terms, where the additive character of the heat of combustion greatly predominates (compare § 5), we see here the structural element of the heat of combustion coming to the fore.

In various other homologous series also and similarly for other properties (refraction, magnetic rotation etc.) we come across a similar deviation in one or more of the initial terms. The question, when and how many initial terms occur with increments in the heat of combustion (refraction increments etc.), which deviate from the normal for the series investigated, has — although it may appear strange — so far never been looked into. We shall soon devote a separate paper to this point.

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