**Chemistry**. — *"The Molecular Heat of Combustion of Successive Terms of Homologous Series"*. By Prof. P. E. Verkade, H. Hartman, and J. Coops Jr. (Communicated by Prof. J. Böeseken).

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The researches published of late on various sides on the alternation of certain physical and physico-chemical constants of the successive terms of different homologous series of organic compounds render it desirable to make a concise communication here on the results of our determinations of the heat of combustion of a number of dibasic acids of the oxalic acid series. Besides we will set forth our working-programme on the subject of heat of combustion of the normal terms of homologous series, hoping that this sphere of action may be left reserved for us.

This communication is, therefore, intended to give only an indication of the main lines along which our work in this field will be conducted in the future. A fuller discussion of the points mentioned here will be found elsewhere.

Already many years ago the first 9 terms ($C_2$ to $C_{10}$ inclusive) of the oxalic acid series were burned with comparatively great accuracy by Stohmann and his collaborators[1]). They found that — as is the case in several homologous series — the first and second term (oxalic acid and malonic acid) occupy a particular place, in so far as the heat of combustion of both is very high compared with that of the other terms of the same series. They further found that the molecular heat of combustion of the higher terms (from succinic acid) did not increase by an almost constant amount of 156 to 157 Cal. for every added $CH_2$-group — as these investigators had found for some other homologous series, or as they have at least believed they had proved; *it was necessary*[2]) *to distinguish in the series of normal saturated dibasic acids two thermal homologous series, one of which comprises the acids with an even number of*

[1]) Stohmann, Kleber and Langbein : Journ. f. prakt. Chem. (2) **40**. 202 (1889); Stohmann and Kleber : ibid. (2) **45**. 475 (1892).

[2]) Cf. Stohmann, Kleber, Langbein and Offenhauer : Verhandl. Sächs. Akad. d. Wiss. **45**. 605 (1893).

*carbon atoms, the other the acids with an odd number of carbon atoms.*

To indicate the place of a compound in a homologous series we shall henceforth introduce the term of *"term number"*, analogous to the term of *"atomic number"* introduced elsewhere. An even term is a term with an even term number. It should be borne in mind that such a term contains an odd number of carbon atoms in the series of the dibasic acids considered here, but on the other hand an even number of carbon atoms in the series of the fatty acids.

We have first determined anew the heat of combustion of the acids examined already by STOHMANN c. s., and we have then continued the series to the $C_{13}$-acid inclusive, in order to bring out the phenomenon still more clearly. The description of the method of preparation of the acids, of the difficulties met with in the combustion of some of these acids, and of the way in which these difficulties were overcome etc. will be given elsewhere. It may only be mentioned here that it is obvious that of every acid at least two preparations had to be burned, the heats of combustion being based on that of benzoic acid of **6324** $cal_{15}°$ per gram (air) [1]) assumed by international agreement.

The following table gives the results obtained by us; the heats

| Term-number | | | Mol. H. of C. in $Cal_{15}°$ | Δ in $Cal_{15}°$ | | |
|---|---|---|---|---|---|---|
| 1 | $C_2$ | oxalic acid | 60.2 | | | |
| | | | | 146.3 | | |
| 2 | $C_3$ | malonic acid | 206.5 | | | |
| | | | | 150.6 | | |
| 3 | $C_4$ | succinic acid | 357.1 | | | |
| | | | | 157.8 | | |
| 4 | $C_5$ | glutaric acid | 514.9 | | $156.0 \times 2$ | |
| | | | | 154.1 | | |
| 5 | $C_6$ | adipic acid | 669.0 | | | $156.4 \times 2$ |
| | | | | 158.7 | | |
| 6 | $C_7$ | pimelic acid | 827.7 | | $157.2 \times 2$ | |
| | | | | 155.7 | | |
| 7 | $C_8$ | suberic acid | 983.4 | | | $157.0 \times 2$ |
| | | | | 158.3 | | |
| 8 | $C_9$ | azelaic acid | 1141.7 | | $157.0 \times 2$ | |
| | | | | 155.6 | | |
| 9 | $C_{10}$ | sebacic acid | 1297.3 | | | $157.0 \times 2$ |
| | | | | 158.3 | | |
| 10 | $C_{11}$ | nonane dicarboxylic acid | 1455.6 | | $156.7 \times 2$ | |
| | | | | 155.1 | | |
| 11 | $C_{12}$ | decane dicarboxylic acid | 1610.7 | | | $156.3 \times 2$ |
| | | | | 157.9 | | |
| 12 | $C_{13}$ | brassylic acid | 1768.6 | | | |

[1]) VERKADE: Chem. Weekblad **19**. 389 (1922).

of combustion given apply to an isothermal reaction at a temperature of about $19°.5$.

The conclusions at which STOHMANN c.s. had arrived, are confirmed in an indeed striking way by our measurements, which were executed with scrupulous care. Oxalic acid and malonic acid actually occupy an exceptional place: the difference in molecular heat of combustion between these two acids and between this latter acid and succinic acid is considerably smaller than that found between any other two successive terms; this fact need not occupy us now any longer, however. We further see that starting with succinic acid, a great and a small combustion heat increment $\Delta$ regularly alternate; the mean values of these two increments — to which, for the rest, we do not wish to assign any significance (see below) — are resp. 158.2 and 155.1 $Cal_{15°}$. If however, we, regard the even and the odd terms as separate series, we find in the two series but little fluctuating combustion heat increments, the means of which amount resp. to $2 \times 156.7$ and to $2 \times 156.7$ $Cal_{15°}$. Hence here two thermal homologous series may be spoken of, that of the acids with even term-number, and with odd term-number. One series is shifted about 1.5 $Cal_{15°}$ with respect to the other.

We wish explicitly to state here that these mean values of the combustion heat increments are given by us merely to elucidate the phenomenon in question, and by no means because we would consider the heat of combustion as an additive quantity, hence the fluctuations in the combustion heat increments as exclusively due to errors of observation. Though in many cases an exceedingly remarkable regularity is observed in the value of the heats of combustion of organic compounds, *it is self-evident that the heat of combustion is without any doubt no additive quantity.*

As yet the series of the normal saturated dibasic acids is the only one in which this phenomenon of the alternation of the combustion heat increments has been observed with certainty. A careful critical examination of the numeric material available in literature has led us to the strong suspicion that a similar alternation of the combustion heat increments is also found at least in the series of *mono-alkylsubstituted malonic acids*, and that this alternation is about of the same order of magnitude. The small number of normal terms, however, of which the heat of combustion has been determined in this case, renders the drawing of a definite conclusion impossible for the present; we intend to undertake the study of this series of acids before long.

Recently Garner and Randall [1]) determined the heat of solidific-
ation (heat of crystallisation) with great accuracy for a number of
normal terms of the fatty-acid series. Their results are recorded in
the subjoined table, which besides gives the most reliable data about
the heat of solidification found in the literature for three other
acids of the same series (marked *).

|  |  | Mol. heat of solidification | Heat of transition $\alpha \longrightarrow \beta$ | Mol. heat of solidification of the $\beta$-form |
|---|---|---|---|---|
| $C_1$ | formic acid * | 2.52 Cal. | | |
| $C_2$ | acetic acid * | 2.77 | | |
| $C_8$ | octylic acid | 5.11 | | |
| $C_9$ | nonylic acid | 4.85 | 1.33 Cal. | 6.17 Cal. |
| $C_{10}$ | decylic acid | 6.69 | | |
| $C_{11}$ | undecylic acid | 6.00 | 1.84 | 7.84 |
| $C_{12}$ | lauric acid | 8.76 | | |
| $C_{14}$ | myristic acid * | 10.84 | | |

Plotting the molecular heats of solidification in a graphical represent-
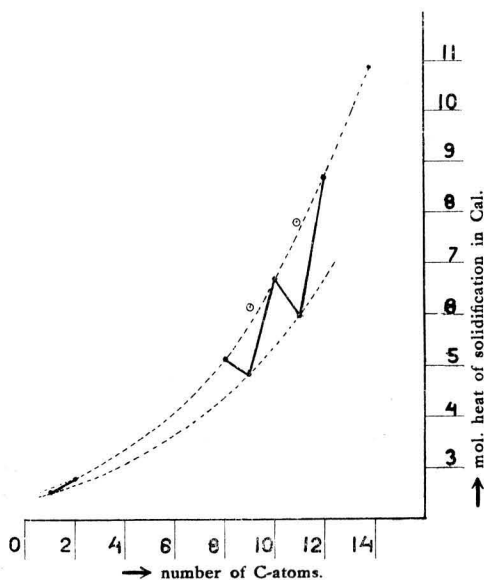ation against the term-number (i.e. against the number of carbon
atoms of the chain), it appears that two continuous curves can
be drawn through the points obtained: on one are situated
all the terms with even term-numbers, on the other all the
terms with odd term-numbers (see fig. 1). *Hence the heat of solidi-
fication of these acids appears to show, in a very typical way,
an alternation in the successive terms of the homologous series.*
Garner and Randall succeeded in showing in an ingenious way
that this alternation is caused by differences in the crystal
structure of the even and odd



Figure 1.

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[1]) Journ. chem. Soc. **125**. 881 (1924). We shall discuss this investigation more
at length on a later occasion.

terms: for they could prove the existence of two enantiotropic forms of the odd terms in two cases (i.e. for nonylic acid and undecylic acid) [1]) and besides establish that the sum of the heats of transition i.e. the heat liberated in the transition from the $\alpha$- into the $\beta$-form, and the heat of solidification of the $\alpha$-form is about equal to the heat of solidification of the $\beta$-form. In the figure the $\beta$-forms of the odd series lie pretty well on the line connecting the even terms of the series; they are marked with ⊙ in the figure.

The considerations on the way of arrangement of the molecules in the crystals of the even and of the $\alpha$- and $\beta$-odd forms given by GARNER and RANDALL in connection with their results, may be left undiscussed here, as not bearing directly on the end we have in view.

Now the question arises whether the oscillation of the combustion heat increments found by us in the *crystalline* normal saturated dibasic acids at 19°.5 must be partially or entirely attributed to a different crystal structure of the even and odd terms.

In order to decide this we should have to compare the molecular heats of combustion found for the crystalline acids with those of the supercooled, liquid acids at the same temperature (19°.5). The difference in molecular heat of combustion between a crystalline acid and the same acid in liquid supercooled condition, both heats of reaction measured for an isothermal reaction at the just-mentioned temperature, is not only determined by the molecular heat of solidification ($s$), but also by the difference in specific heat of the acid in the solid and in the supercooled liquid condition ($v$) [2]) and by the position of the melting-point ($t$). For an acid of molecular weight $M$ this difference is:

$$V = s + M v (t - 19.5)$$

in which it may still only be pointed out here that $v$ can be both positive and negative. If in the case of normal saturated dibasic acids in the liquid state the regular oscillations of the combustion heat increments are to disappear entirely, *the general condition is that both in the series of the even terms and in that of the odd ones the difference V shall increase from term to term by a constant amount equal for the two series.*

Let us first consider the following special case. In many homolo-

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[1]) Cf. TAMMANN: Zeitschr. f. anorg. Chem. **109**. 221 (1923).

[2]) For simplicity a possible variation of the specific heat with the temperature has been left out of account here.

gous series — also in the series in question — the melting-points
of the successive terms show likewise a typical oscillation. Besides
they present the peculiarity that when we get higher in the series
the melting-points approach each other more and more. We may
now imagine the theoretical case that a number of successive high
terms of a homologous series have all almost the same melting-point;
we then consider the isothermal heat of combustion of the solid state
and of the liquid state at the temperature of the melting-point. The
difference between these two molecular heats of combustion for each
term then amounts to:

$$V' = s.$$

If further we suppose the molecular combustion heat increments
for the crystalline substances between an odd term and the next
even term to be always 158.2 Cal., and between the latter and the
next odd term to be always 155.1 Cal. — i. e. if for a moment
we suppose a pure additivity of the heat of combustion, the following
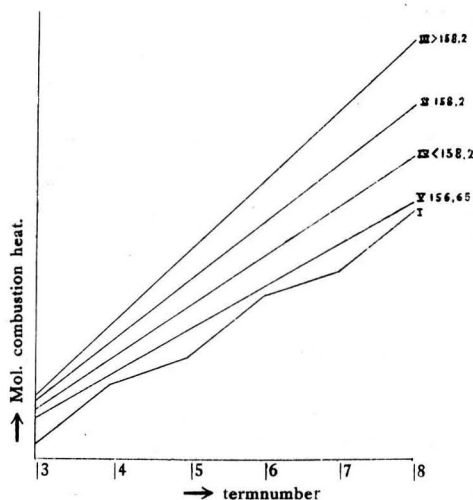interesting relations may be derived.



Figure 2.

*A general condition for the
total disappearance of the oscil-
lations in the liquid state is that
both in the series of the even terms
and in that of the odd terms
the molecular heat of solidifica-
tion increases from term to term
by a constant amount equal for
the two series.* When the mole-
cular heats of solidification and
the *term-numbers* are joined in a
graphical representation, we get
two straight, parallel lines.

There is now a close relation
between the angle of inclination
of these solidification-heat lines, their mutual position, and the value
of the combustion heat increment of the substances in the liquid state.
A full discussion of this relation will be given elsewhere. Here we will
only point out the following conclusions, which can be easily derived
by the aid of fig. 2, in which line I diagrammatically represents
the course of the heat of combustion of the crystalline substances.

1. If the increment of heat of combustion for the liquid substances
is **exactly 158.2** Cal. (line II), the heat of solidification of every even
term is equal to that of the preceding odd term.

2. If this increment is *greater than* 158.2 *Cal.* (line III), the heat of solidification of an even term is greater than that of the preceding odd term; if it is *smaller than* 158.2 *Cal.*, the heat·of solidification of the even terms is always smaller than that of the preceding odd term (line IV).

3. If this increment is **156.65 Cal.**, i. e. exactly the mean of the values of 158.2 and 155.1 Cal., the heat of solidification is constant for all the even and for all the odd terms (line V).

4. A still smaller increment of the heat of combustion for the liquid substances than 156.65 Cal. leads from any term of the homologous series to negative heats of solidification; *hence it is impossible.*

Let us now for a moment return to the general case. Here the same relations are valid, provided the differences $V$ be substituted for the heats of solidification. This case, too, will be discussed more at length elsewhere.

The slight fluctuations which each of the two series of combustion heat increments of the crystalline acids presents in our case, bring no change at all in the general aspect of these relations. Which of the possibilities 1—3 will occur here, cannot be said with certainty a priori; on the ground of the increment for the $CH_2$-group found in other series of liquid compounds it seems probable that here the combustion heat increment of this group will appear to lie below about 158.2 and above about 156.7 Cal.

The same considerations are valid for the mono-alkylmalonic acids discussed above, if actually the same phenomenon of oscillation should be found to exist in these crystalline acids as in the acids of the oxalic acid series.

Without any doubt the heat of solidification and also the specific heat of the melted (resp. supercooled) acid cannot be determined for most of the dibasic acids of the two series discussed, among others on account of anhydrisation, resp. splitting off of carbonic acid during the heating. In the first place we therefore set ourselves the task to determine, by way of expedient, the heat of combustion of series of liquid derivatives of these acids, e.g. of *ethylesters*, and especially of *methylesters*, in order to decide whether, and if so in how far, there still exists an alternation of the combustion heat increments. In some cases the heats of combustion of the solid and the liquid state of the methylesters can be both determined directly by working in an adiabatic calorimetric system at different temperatures, the heats of solidification and the specific heats being

also measurable here. Hence we can form a complete idea of the state of things at least in these few cases. If these liquid derivatives should show an almost constant combustion heat increment, it would have been rendered probable, at least to some extent, by an indirect way *that the periodicity of these increments in the crystalline acids is due to differences in the crystalline structure of the even and the odd terms.*

It is still quite an open question whether perhaps all homologous series of crystalline compounds show periodicity of the combustion heat increments *in a more or less pronounced degree.* It is of course by no means a priori necessary then that in all cases — as this is the case with the acids of the oxalic acid series — two unequal, but both almost constant combustion heat increments, regularly alternate. This problem will be investigated by measurements on different series of homologues (preferably such for which also a measurement of the heats of solidification and of the specific heats of the solid and the liquid state is possible) for the particular purpose of ascertaining the constitutive influences, which either produce, or strengthen, resp. weaken these oscillations.

The material of facts concerning the heats of combustion of the normal saturated dibasic acids used in this communication has been collected by the second of us (H.).

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