LIV.—The Boiling Points of Homologous Compounds. Part II.

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In a previous communication (this vol., p. 193), I showed that it is possible to express the boiling points of any one series of the normal ethers by means of the formula

$$T = aM^b,$$

in which T is the boiling point measured in the absolute scale of temperature, M the molecular weight, and a and b constants for the series, with values varying from series to series.

I have now extended the application of the formula to other groups of compounds, and in the present paper communicate the results I have obtained.

The first class of substances examined were the ethereal salts of the normal fatty acids, which in many of their physical properties present close analogies to the ethers, and so might be expected to fall under the same type of boiling-point formula as is valid for the latter. This I found to be actually the case, as the following tables will suffice to show. The data used were those given by Beilstein in his *Handbuch*, and by Gartenmeister (*Annalen*, 233, 294). Occasionally, the divergences between the boiling points found by different observers are considerable, and in such cases I have either taken the mean of the various values, or selected that which from internal evidence appeared the most trustworthy.

Methylic salts of Normal Fatty Acids.

$$T = 38.28 M^{0.4937}.$$

Acid.	t .	T .	T (calc.).	Difference.
Acetic	57.3°	330.3	320.5	-9.8
Propionic	79.5	352.5	349.1	-3.4
Butyric	102.3	375.3	375.5	+0.2
Valeric	127.3	400.3	400.1	-0.2
Caproic	149.6	422.6	423.2	+0.6
Heptylic	172.1	445.1	445.1	0
Octylic	192.9	465.9	466.1	+0.2
Nonylic	213.0	486.0	486.1	+0.1

Here, in the case of the methylic ethereal salts, we have exactly the same behaviour as was observed with the methyl ethers (*loc. cit.*, p. 197): the formula which applies to the higher members of the series gives quite erroneous values for the first two members.

Ethylic Salts.

$$T = 37.76 M^{0.4937}.$$

Acid.	<i>t.</i>	T.	T (calc.).	Difference.
Acetic.....	77.5°	350.5	344.3	-6.2
Propionic.....	98.8	371.8	370.4	-1.4
Butyric.....	120.9	393.9	394.6	+0.7
Valeric.....	144.7	417.7	417.4	-0.3
Heptylic.....	166.6	439.6	439.0	-0.6
Octylic.....	187.1	460.1	459.7	-0.4
Nonylic.....	205.8	478.8	479.4	+0.6
Decylic.....	{ 216—219 227—228	{ 489—492 500—501	} 498.3	?
Undecylic.....				
	244	517	516.4	-0.6

Here the first member alone is decidedly abnormal in its boiling point.

Propylic Salts.

$$T = 37.76 M^{0.4937}.$$

Acid.	<i>t.</i>	T.	T (calc.).	Difference.
Acetic.....	101.8°	374.8	370.3	-4.5
Propionic.....	122.6	395.6	394.7	-0.9
Butyric.....	143.2	416.2	417.4	+1.2
Valeric.....	167.5	440.5	439.0	-1.5
Caproic.....	185.5	458.5	459.7	+1.2
Heptylic.....	206.4	479.4	479.4	0
Octylic.....	224.7	497.7	498.3	-0.6

The data for the propylic salts are very unsatisfactory, the differences between the values given by Gartenmeister and those of other observers often amounting to several degrees. This accounts for the comparatively large differences found between the calculated and observed boiling-points, a fact further borne out by the irregular distribution of the + and - signs amongst these differences, which indicates a large experimental error.

When we compare the constants for the three series we find that they are as follows:—

	Methyl.	Ethyl.	Propyl.
<i>a</i>	38.28	37.76	37.76
<i>b</i>	0.4937	0.4937	0.4937

The constant a varies very little, whilst b remains absolutely the same. The identity of the values of a in the case of the ethylic and propylic series is no doubt accidental, and due to the faulty data for the propylic salts.

When two series have exactly the same constants, the isomeric substances belonging to them have the same boiling-point; thus, for example, propylic propionate should have the same boiling-point as ethylic butyrate. We find, on comparing the two series, that the differences amount to more than a degree and are irregular, being sometimes positive and sometimes negative, in accordance with the general irregularity exhibited by the propylic salts.

A consequence of the very small variations of the constants for the different series is that, when we arrange the ethereal salts in series according to their acids, they should then come under a formula with practically the same constants. I have therefore calculated the values for the alkyl acetates, and the following table will serve to show that this indeed occurs, the two first members being again exceptional.

Alkyl Acetates.

$$T = 38.11 M^{0.4937}.$$

Alkyl.	t .	T .	T (calc.).	Difference.
Methyl	57.3°	330.3	319.0	-11.3
Ethyl	77.5	350.5	347.5	-3.0
Propyl.	101.8	374.8	373.8	-1.0
Butyl	124.4	397.4	398.3	+0.9
Amyl.	148.4	421.4	421.3	-0.1
Hexyl	169.2	442.2	443.0	+0.8
Heptyl	191.5	464.5	464.0	-0.5
Octyl	210	483	483.8	+0.8

The value of b was chosen equal to that previously found, and it will be seen that the resulting value of a is intermediate between the values for the methylic and ethylic series.

As the boiling point at the atmospheric pressure is only one particular example selected from the range of possible boiling points, I thought it of interest to determine whether the formula $T = aM^b$ is valid for boiling points at pressures other than that of the atmosphere. Some data for the boiling points of ethereal salts of fatty acids, at different pressures, are given by Schumann (Wiedmann's *Annalen*, 12, 40), and these were sufficient to show that the formula is not only valid, but that the constant b still retains its value unchanged, and that a varies very little from series to series. I do not here reproduce the tables calculated by me, as the data are only for short series, and I shall give examples of longer series in the case of the hydrocarbons.

An interesting deduction, however, may be drawn from the constancy of b at different pressures. If we take two substances belonging to the same series, we have for their boiling points, at a certain pressure, p ,

$$T = aM^b \text{ and } T_1 = aM_1^b.$$

At another pressure, p' , we have the boiling points

$$T' = a'M^b \text{ and } T'_1 = a'M_1^b.$$

M , M_1 , and b remain the same throughout; so, by dividing each equation of the first pair by the corresponding equation of the second pair, we obtain

$$\frac{T}{T'} = \frac{a}{a'} \text{ and } \frac{T_1}{T'_1} = \frac{a}{a'}, \text{ whence } \frac{T}{T'} = \frac{T_1}{T'_1}.$$

That is, if b remains constant for different pressures, the ratio of the boiling points (expressed in the absolute scale) at any two given pressures will remain the same for all members of the homologous series. The following tables, compiled from Schumann's data, show the accuracy of this deduction in the case of the ethereal salts of the fatty acids.

Formates.

Alkyl.	B. p. at 1300 mm.	B. p. at 200 mm.	Ratio.
Methyl.....	320.1	273.7	0.855
Ethyl.....	343.2	293.1	0.854
Propyl.....	371.3	318.0	0.856
(Isobutyl).....	388.8	332.4	0.855
Amyl.....	416.7	356.2	0.855

Acetates.

Alkyl.	B. p. at 1300 mm.	B. p. at 200 mm.	Ratio.
Methyl.....	346.0	296.5	0.857
Ethyl.....	367.3	314.4	0.856
Propyl.....	392.2	336.1	0.857
(Isobutyl).....	408.5	349.6	0.856

Propionates.

Alkyl.	B. p. at 1300 mm.	B. p. at 200 mm.	Ratio.
Methyl.....	370.0	316.7	0.856
Ethyl.....	389.9	333.7	0.856
Propyl.....	414.7	355.0	0.856
(Isobutyl).....	429.9	368.0	0.856
Amyl.....	454.2	389.9	0.858

It will be observed that the ratios are not only the same in each series, but are the same for all the series. This depends on the very slight variability of the constant a in the various series of the

etheral salts, for if a and a' differ but little from series to series, the ratio a/a' will remain sensibly constant.

Ramsay and Young (*Phil. Mag.*, **21**, 33 and **22**, 37) found that if T and T_2 were the absolute boiling points of any two substances at a pressure p , T' and T_1' their boiling points at a pressure p' , the following relation held good.

$$\frac{T'}{T_1'} = \frac{T}{T_1} + c(T' - T).$$

In the case of closely related substances the constant c becomes zero, so that the relation assumes the form

$$\frac{T'}{T_1'} = \frac{T}{T_1},$$

that is, the ratio of the boiling points of such substances is independent of the pressure. This relation is the same as that which was deduced for the ethereal salts from a consideration of the formula

$T = aM^b$, for, if in the proportion $\frac{T}{T_1} = \frac{T_1}{T_1'}$, we interchange the

means, we obtain $\frac{T}{T_1} = \frac{T'}{T_1'}$, Ramsay and Young's formula.

The fatty acids exhibit regularly decreasing differences of boiling point as the series is ascended, so that it appeared not improbable that they would fall under the formula $T = aM^b$, although with them the constants would have to assume very different values from those of their ethereal salts. This is borne out by the following table.

Normal Fatty Acids.

$$T = 103.275 M^{0.322}.$$

Acid.	t .	T .	T (calc.).	Difference.
Acetic	118.0°	391.0	386.0	-5.0
Propionic	140.6	413.6	412.9	-0.7
Butyric	163.2	436.2	436.6	+0.4
Valeric	184.5	457.5	457.9	+0.4
Caproic	204.5	477.5	477.3	-0.2
Heptylic	223	496	495.1	-0.9
Octylic	237	510	511.7	+1.7
Nonylic	254	527	527.2	+0.2

The divergence in the case of octylic acid is almost certainly due to an error of observation.

A very extensive material for the application of the formula is offered by the normal saturated hydrocarbons, whose boiling points were determined at several different pressures by Krafft. It at once became evident that the formula is not valid for the whole range

from CH_4 to $\text{C}_{19}\text{H}_{40}$, but for a range of 10 hydrocarbons it can be applied with success, so that in this respect it is on at least an equal footing with other formulæ which have been proposed, and superior to them in point of simplicity. In this particular case the formula is unusually simple, for the constant b becomes equal to 0.5, the curve of boiling points being, therefore, a true parabola. Not only is the value of b equal to 0.5 at the atmospheric pressure, but, as with the ethereal salts, this value may be retained for other pressures.

Normal Paraffins at 760 mm.

$$T = 37.38 M^{0.5}.$$

Hydrocarbon.	t .	T.	T (calc.).	Difference.
C_7H_{16}	100.5°	373.5	373.8	+0.3
C_8H_{18}	125.5	398.5	399.1	+0.6
C_9H_{20}	149.5	422.5	422.9	+0.4
$\text{C}_{10}\text{H}_{22}$	173	446	445.5	-0.5
$\text{C}_{11}\text{H}_{24}$	194.5	467.5	466.8	-0.7
$\text{C}_{12}\text{H}_{26}$	214.5	487.5	487.2	-0.3
$\text{C}_{13}\text{H}_{28}$	234	507	507.3	+0.3
$\text{C}_{14}\text{H}_{30}$	252.5	525.5	526.0	+0.5
$\text{C}_{15}\text{H}_{32}$	270.5	543.5	544.1	+0.6
$\text{C}_{16}\text{H}_{34}$	287.5	560.5	561.9	+1.4

In this table, as in the other tables for the hydrocarbons, where the boiling points are not known with accuracy to less than a degree, the decimals of a degree in the calculated values are only approximate, and may be 0.2 or 0.3 out in extreme cases. To show how far the formula diverges from the true values at the worst, it may be mentioned that the boiling point of methane as calculated is -123° , observed value being given as -155° to -160° .

The pressures at which the boiling points of the hydrocarbons were

Normal Paraffins at 15 mm.

$$T = 28.53 M^{0.5}.$$

Hydrocarbon.	t .	T.	T (calc.).	Difference.
$\text{C}_{12}\text{H}_{26}$	98 °	371	371.9	+0.9
$\text{C}_{13}\text{H}_{28}$	114	387	387.2	+0.2
$\text{C}_{14}\text{H}_{30}$	129.5	402.5	401.5	-1.0
$\text{C}_{15}\text{H}_{32}$	144	417	415.4	-1.6
$\text{C}_{16}\text{H}_{34}$	157.5	430.5	429.0	-1.5
$\text{C}_{17}\text{H}_{36}$	—	—	442.0	—
$\text{C}_{18}\text{H}_{38}$	181.5	454.5	454.8	+0.3
$\text{C}_{19}\text{H}_{40}$	193	466	467.0	+1.0
$\text{C}_{20}\text{H}_{42}$	205	478	479.2	+1.2

Normal Paraffins at 30 mm.

$$T = 29.68 M^{0.5}.$$

Hydrocarbon.	<i>t.</i>	T.	T (calc.).	Difference.
C ₁₁ H ₂₄	96.5°	369.5	370.7	+1.2
C ₁₂ H ₂₆	113.8	386.8	386.9	+0.1
C ₁₃ H ₂₈	130	403	402.9	-0.9
C ₁₄ H ₃₀	145.5	418.5	417.7	-0.8
C ₁₅ H ₃₂	160	433	432.1	-0.9
C ₁₆ H ₃₄	174	447	446.3	-0.7
C ₁₇ H ₃₆	187.5	460.5	459.8	-0.7
C ₁₈ H ₃₈	200	473	473.2	+0.2
C ₁₉ H ₄₀	212	485	485.8	+0.8

Normal Paraffins at 50 mm.

$$T = 30.56 M^{0.5}.$$

Hydrocarbon.	<i>t.</i>	T.	T (calc.).	Difference.
C ₁₀ H ₂₂	90°	363	364.1	+1.1
C ₁₃ H ₂₈	142.5	415.5	414.9	-0.6
C ₁₄ H ₃₀	158	431	430.1	-0.9
C ₁₅ H ₃₂	173	446	445.1	-0.9
C ₁₆ H ₃₄	187.5	460.5	459.6	-0.9
C ₁₇ H ₃₆	201.5	474.5	473.5	-1.0
C ₁₈ H ₃₈	214.5	487.5	487.2	-0.3
C ₁₉ H ₄₀	226.5	499.5	500.3	+0.8

Normal Paraffins at 100 mm.

$$T = 32.03 M^{0.5}.$$

Hydrocarbon.	<i>t.</i>	T.	T (calc.).	Difference.
C ₁₁ H ₂₄	127°	400	400.0	0
C ₁₂ H ₂₆	145.5	418.5	417.6	-0.9
C ₁₃ H ₂₈	162.5	435.5	434.8	-0.7
C ₁₄ H ₃₀	178.5	451.5	450.8	-0.7
C ₁₅ H ₃₂	194	467	466.3	-0.7
C ₁₆ H ₃₄	208.5	481.5	481.6	+0.1
C ₁₇ H ₃₆	223	496	496.3	+0.3
C ₁₈ H ₃₈	236	509	510.6	+1.6
C ₁₉ H ₄₀	248	521	524.3	+3.3

observed by Krafft are 15 mm., 30 mm., 50 mm., and 100 mm., as well as the atmospheric pressure of 760 mm., so that here the formula may be put to a somewhat severe test of its applicability. In the above tables the value of *b* has been made equal to 0.5, and it will

be seen that even with this restriction the formula accords fairly well with the facts, and the agreement is little better when b is allowed to vary from pressure to pressure.

The variation in the value of the constant a may be seen in the accompanying table

Pressure.	15 mm.	30 mm.	50 mm.	100 mm.	760 mm.
a	28.53	29.68	30.56	32.03	37.38

Of the monhalogen derivatives of the normal paraffins it is only the chloro-compounds which have boiling points in accordance with the expression $T = nM^b$; the alkyl bromides and iodides show large divergences. The chlorides are exceptional inasmuch as the formula holds good for the first member of the series as well as for the others.

Alkyl Chlorides.

$$T = 27.65 M^{0.561}.$$

Chloride.	t .	T .	T (calc.).	Difference.
CH_3Cl	-23.7°	249.3	249.6	+0.3
$\text{C}_2\text{H}_5\text{Cl}$	+12.5	285.5	286.3	+0.8
$\text{C}_3\text{H}_7\text{Cl}$	46.4	319.4	319.7	+0.3
$\text{C}_4\text{H}_9\text{Cl}$	78.0	351.0	350.5	-0.5
$\text{C}_5\text{H}_{11}\text{Cl}$	106.6	379.6	379.3	-0.3
$\text{C}_6\text{H}_{13}\text{Cl}$	133	406	406.5	+0.5
$\text{C}_7\text{H}_{15}\text{Cl}$	159.2	432.2	432.4	+0.2
$\text{C}_8\text{H}_{17}\text{Cl}$	183	456	457.1	+0.1

The data for the normal alkylamines, although extensive, are unsatisfactory owing to the considerable differences in the boiling points obtained by different observers. They are sufficient to show, however, that the formula $T = aM^b$ may be applied to them with fair success. Owing to the great divergences observed, I have simply calculated the values to the nearest degree, the error of observation being certainly much greater than that value.

A simple inspection of the differences between the boiling points of successive alcohols suffices to show that no formula of the type of $T = aM^b$ can possibly be applied to them, for instead of these differences diminishing continually, they increase, reach a maximum, decrease, and apparently again increase if the observed boiling points of the highest alcohols are to be relied on. It is well known that compounds containing the hydroxyl group are exceptional in their behaviour in many respects, and this peculiar conduct is usually

Normal Alkylamines.

$$T = 58.48 M^{0.413}.$$

Base.	<i>t</i> .	T.	T (calc.).	Difference.
CH ₃ ·NH ₂	- 6°	267	246	-21
C ₂ H ₅ ·NH ₂	+ 18	291	287	- 4
C ₃ H ₇ ·NH ₂	49	322	322	0
C ₄ H ₉ ·NH ₂	76	349	351	+ 2
C ₆ H ₁₃ ·NH ₂	103	376	378	+ 2
C ₆ H ₁₃ ·NH ₂	129	402	402	0
C ₇ H ₁₅ ·NH ₂	153	427	425	- 2
C ₈ H ₁₇ ·NH ₂	173	446	446	0
C ₉ H ₁₉ ·NH ₂	191	464	465	+ 1
C ₁₂ H ₂₅ ·NH ₂	248	520	519	- 1

attributed to the polymerisation of their molecules in the liquid state, a view which receives direct confirmation from the recent work of Ramsay and Shields on surface tension. It is therefore not surprising if the liquid molecules are more complex than the gaseous molecules, and that in different degrees from member to member of the series, that they should come under no simple formula for the boiling point, as this temperature must be held to depend directly on the mass of the liquid molecule. It might be objected, in opposition to this view, that a similar explanation is not needed for the fatty acids, which do come under the formula $T = aM^b$, although they contain hydroxyl. But, as Guye has pointed out, the two cases differ entirely, inasmuch as the *vapours* of the acids at their boiling points are associated, and probably to approximately the same degree as the liquids, whilst the vapours of the alcohols show no trace of molecular association.

From the experiments of Ramsay and Shields, it is evident that the amount of association of the alcohols decreases as the series is ascended, and I have found that, starting from amyl alcohol, it is possible to apply the formula $T = 85.45 M^{0.350}$ to the series with an error within the error of experiment. As the data, however, are rather meagre and uncertain, I do not reproduce the table here.

The boiling points of the nitriles of the fatty acids have not been very accurately determined, but the formula $T = 119.6 M^{0.282}$ gives fair results with those whose boiling points are well known. It should be mentioned that propionitrile yields values for surface tension which indicate that it is considerably associated in the liquid state.

The data for the normal acid chlorides and the mercaptans are so scanty and untrustworthy that almost any form of expression may be

used for their boiling points without going beyond the limit of the experimental error.

The boiling points of the normal simple ketones are expressed by the formula $T = 63.39 M^{0.4}$ so far as the existing data allow us to judge. The same formula may be used for the normal saturated aldehydes, the boiling points, however, again varying very much according to the observer. The following table will give an idea of the accuracy of the results in such cases.

Normal Aldehydes.

$$T = 63.39 M^{0.4}$$

Aldehyde.	<i>t.</i>	<i>T.</i>	<i>T</i> (calc.).
Acetic	21°	294	288
Propionic	49—50	322—323	322
Butyric	73—77	346—350	351
Valeric	102—103	375—376	376
Caproic	128	401	400
Oenanthic	150—156	423—429	422

The foregoing tables include all the series of any length for which even moderately trustworthy boiling-point data can be obtained. They show that, for well-determined series in which no association of the liquid molecules is known to take place, the formula $T = aM^b$ is valid, except in the series of the alkyl bromides and iodides. In a very long series, such as that of the hydrocarbons (with 19 members), the same constants cannot be used with strictness for the whole series, but only for a portion of it (about 10 members).

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