On the Boiling Points of Organic Compounds. I. The Formula of BoggiaLera

A. H. W. Aten Jr.

Citation: The Journal of Chemical Physics **5**, 260 (1937); doi: 10.1063/1.1750016
View online: http://dx.doi.org/10.1063/1.1750016
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/5/4?ver=pdfcov
Published by the AIP Publishing

On the Boiling Points of Organic Compounds. I. The Formula of Boggia-Lera

A. H. W. Aten, Jr.
Hilversum, Netherlands
(Received, January 6, 1937)

ALTHOUGH the boiling point of the more complicated compounds, such as those we usually find among organic substances, depends on a number of different properties of the molecule, the exceptional practical importance of this quantity makes it worthwhile to establish empirical methods for calculating its value. Our starting point will be the fact, which was discovered by Young,[1] that the increase of the boiling point per CH_2 group in different homologous series is determined by the boiling point of the substance to which the methylene group is added alone, independently of its structure and composition. This rule, which holds with surprising accuracy except in the case of associated liquids like acids or alcohols, was expressed by Young in the following formula, in which Δ_T indicates the increase in boiling point on the introduction of one CH_2 group and T_B the boiling point in degrees absolute.

$$\Delta_T = \frac{144.86}{T_B{}^{0.0148\sqrt{T_B}}}. \tag{1}$$

Young remarks that this formula does not apply to the first members of a series; it can only be used for compounds which contain the configuration $-C-C-C-$. As we shall make use of the fact, that Δ_T is determined by T_B, we shall have to restrict ourselves to substances which contain three carbon atoms. It is clear that the Young formula cannot be used to express the boiling points of an entire series in one mathematical expression, which makes its application very cumbersome.

For this reason we shall go back to a formula proposed by Boggia-Lera[2] for the monoderivates of the paraffin series. It says that the square of the boiling points of a homologous series expressed in degrees Kelvin form a linear function of the molecular weight, or, which is the same, of the number of CH_2 groups. We shall write this formula:

$$T = (n \cdot D + B)^{\frac{1}{2}}, \tag{2}$$

n being the number of CH_2 groups in the molecule, D and B are constant in a given series. From the fact that the increase of T with n is dependent on T only, one easily concludes that D must have the same value for every homologous series. This is not exactly what Boggia-Lera found, but the variation in his values of D is small, and besides it is seen from the consideration of a series in which a great number of boiling points are known, like the paraffins, that D is not quite constant, and that therefore the value computed depends more or less on the number of substances considered. Table I[3] shows that the value $D = 20{,}500$ fits most of the paraffins and their monoderivates quite accurately. Only the highest members of the paraffin series show considerable deviations. The calculated values for the boiling points of molecules which do not contain the configuration $-C-C-C-$ are shown between brackets; in most of these cases the agreement is very poor, the paraffins and alkylhalides being exceptions. It must be specially pointed out, that the reasons for the validity of our empirical formula (2) are various and of a complicated nature. We hope to deal with these theoretical considerations in a later paper but in this connection we want to stress the fact that we have no reason to assume that our formula will hold with any accuracy outside the range for which we have ascertained its validity.

After proving the applicability of formula (2) with the value 20,500 for D in the case of monoderivates of paraffins we must investigate whether it can also be used for other compounds. Adequate data are available for paraffin derivates bearing a group at each end and for those having a substituent in the middle. In both cases our

[1] Young, Phil. Mag. **9**, 1 (1905).
[2] E. Boggia-Lera, Gazz. chim. Ital. **29**, 1, 441 (1899).
[3] The data are taken from Beilstein and from Wakeman, Rec. **53**, 832 (1934).

formula applies, within the limitations mentioned before, as shown in Tables II and III.

Now the only matter left for consideration is the value of the constant B in different series. As all series considered in Table I and II are different only in the end groups, it is logical to ascribe to these end groups the differences in B. It is found that the values for this constant are roughly additive as a function of the two end groups. If we take the value for H as one-half of the B in the paraffin series, we can calculate all B's for the substances in Table I. In Table IV the values found in this way, marked I are compared to the values found by halving the con-

TABLE I. $T=(n\cdot 20{,}500+B)^{\frac{1}{2}}$.

	Paraffins $H(CH_2)_nH$ $B=-7000$		Olefines $H(CH_2)_n-CH=CH_2$ $B=31000$		Alkyl-acetylenes $H(CH_2)_n-C\equiv CH$ $B=40000$		2-methyl Paraffins $H(CH_2)_n-CH(CH_3)_2$ $B=49500$		Methyl-alkyl-acetylenes $H(CH_2)_n-C\equiv C-CH_3$ $B=67000$		Alkyl-monochlorides $H-(CH_2)_nCl$ $B=41000$	
n	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T
1	(116)	112	227	225	246	250	264	263	296	301	(248)	249
2	(184)	185	268	268	285	291	301	304	329	328	(286)	285
3	233	228	304	303	319	313	333	334	358	359	320	320
4	274	274	336	337	349	344–345	363	363	386	386	351	351
5	309	309	365	367	377	373	390	390	412	411	379	379
6	341	342	392	394–395	404	400–401			436	434	405	407
7	370	371	418	419	428	424–425					453	458
8	397	398	442	441								
9	421	424	464	461–463								
10	445	447										
11	467	470										
12	489	489										
13	509	507										
14	530	525										
15	548	543										
16	567	560										
17	584	576										
18	602	590										
19	618	603										

	Alkyl-monobromides $H(CH_2)_nBr$ $B=57500$		Alkyl-monojodides $H(CH_2)_nI$ $B=80500$		Methyl Ethers $H(CH_2)_nOCH_3$ $B=35500$		Alkyl Formates $HCOO(CH_2)_nH$ $B=62000$		Methyl Esters $H(CH_2)_nCOOCH_3$ $B=79000$		Mercaptans $H(CH_2)_nSH$ $B=55000$	
n	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T
1	(279)	278	(318)	316	(237)	248	(287)	305	(315)	330	(275)	279
2	(314)	311	(349)	345	(277)	284	(321)	327	347	353	(310)	310
3	345	344	377	375	312	312	351	354	375	375	341	340
4	374	364?	403	400	343	344	379	380	401	400	370	370
5	400	403	428	429	372	372–373	406	403	426	423	397	399
6	425	429	451	453			430	427	449	446	422	420
7					423	423	453	450	472	466	447	447
8			494	498	447	446	475	471	493	486–487		
9									513	496–497		
10												
11												
12												
13									579	568		
14												
15												
16												
17									646	715–716?		

TABLE II. $T=(n\cdot 20{,}500+B)^{\frac{1}{2}}$.

	Dimethyl Paraffins $(CH_3)_2CH(CH_2)_n-CH(CH_3)_2$ $B=105000$		Alkyl Dichlorides $Cl(CH_2)_nCl$ $B=100000$		Alkyldibromides $Br(CH_2)_{n2}Br$ $B=137000$		Dimethyl Ethers $CH_3O(CH_2)_nOCH_3$ $B=81000$		Dimethyl Dicarboxylesters $CH_3OOC(CH_2)_n-COOCH_3$ $B=17700$	
n	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T
1	354	358–359	(347)	313	(397)	371	319	318	444	454
2	382	382	(375)	357	(422)	404	349	~355	467	465
3	408	406	402	398	446	441			488	487
4	432	433	427	434–436?	468	470–471	404	405–406		
5			450	453	489	493–495	428	429–432		
6			472	476–478	510	512–514	453	453	547	541
7					530	536	473	474		
8							495	494		
9			514	513–515						
10			533	531–535						

stants used in Table II (which are marked II), and the average values are shown between brackets. Insofar as this additivity holds we can state the following rule:

"The square of the boiling points of an organic compound consisting of a chain of at least 3 carbon atoms with two end groups is an approximately additive quantity, which can be calculated by adding a certain characteristic value for each methylene and end group." In Table V the boiling points for a number of compounds are calculated from this rule.

Formula (2), although it is not quite exact, can help us to information about the so-called "replacement values" of boiling points; the change which occurs in the boiling points of a substance on substitution of one group for another. Smiles[4] remarks on the fact that such a "replacement value" decreases with increasing term number and expresses the opinion that it may ultimately become constant. From our formula we are indeed led to expect a constant difference between the squares of the absolute boiling points, which means that the difference between the boiling points of two compounds

TABLE III. $T=(n\cdot 20{,}500+B)^{\frac{1}{2}}$.

	Methyl paraffins $H(CH_2)_{n/2}-C(CH_3)(CH_2)_{n/2}H$ $B=28000$		Dialkylethers $H(CH_2)_{n/2}O(CH_2)_{n/2}H$ $b=8000$	
n	T_{calc}	T	T_{calc}	T
2	265	263	(221)	249
4	333	337	(300)	308
6	390	391	362	364
8	439	438	415	414
10				
12			543	535
14			580	565

[4] Smiles, *Chemical Constitution and Physical Properties*, p. 225.

TABLE IV.

End Group	B value
H	−3500
$-CH=CH_2$ I	34500
$-C\equiv CH_2$ I	43500
$-CH(CH_3)_2$ I	53000
II	52000
	(52500)
$-C\equiv C-CH_3$ I	70500
−Cl I	44500
II	50000
	(47000)
−Br I	61000
II	68500
	(64500)
−I I	84000
$-OCH_3$ I	39000
II	40500
	(39500)
−OOCH	65500
$-COOCH_3$ I	82500
II	88500
	(85500)
−SH	55000

with the same term number is inversely proportional to the sum of the two boiling points. Thus the replacement value does decrease with increasing term number, but can never reach a limiting value, so long as formula (2) holds.

TABLE V.

MOLECULE	T_{calc}	T
$Cl(CH_2)_3Br$	417	415
$Cl(CH_2)_3OCH_3$	385	384
$Br(CH_2)_3OCH_3$	407	405
$I(CH_2)_3OCH_3$	430	431
$CH_3O(CH_2)_3COOCH_3$	432	436
$Cl(CH_2)_3COOCH_3$	441	436–439
$Br(CH_2)_3COOCH_3$	460	459–460
$I(CH_2)_3COOCH_3$	481	471–473
$(CH_3)_2CH(CH_2)_2Cl$	375	373
$(CH_3)_2CH(CH_2)_2Br$	397	392
$(CH_3)_2CH(CH_2)_2I$	421	420
$(CH_3)_2CH(CH_2)_3Cl$	401	398–399
$(CH_3)_2CH(CH_2)_3Br$	422	316–320
$(CH_3)_2CH(CH_2)_2CH=CH_2$	358	358
$(CH_3)_2CH(CH_2)_3CH=CH_2$	385	384–388
$CH_2=CH(CH_2)_2CH=CH_2$	332	332
$(CH_3)_2CH(CH_2)_2C\equiv CH$	370	365–366
$CH_2=CH(CH_2)_2C\equiv CH$	345	343
$CH\equiv C(CH_2)_2C\equiv CH$	358	359
$CH_2=CH(CH_2)_2OCH_3$	339	341–342
$(CH_3)_2CH(CH_2)_2OCH_3$	365	364
$(CH_3)_2CH(CH_2)_2OOCH$	399	396
$(CH_3)_2CH(CH_2)_3COOCH_3$	447	440
$(CH_3)_2CH(CH_2)_2SH$	385	389–393

TABLE VI. *Cycloparaffins* $(CH_2)_n$. $T=(n\cdot 24{,}300-18{,}000)^{\frac{1}{2}}$.

n	T_{calc}	T
3	234	238
4	286	284–285
5	322	323
6	358	353
7	390	392
8	420	422
9	448	444
10	474	474

Finally, we must point out that the cycloparaffins cannot be expected to show the same dependence of Δ_T on T_B as the paraffins and their derivates do, because the position of the hydrogen atoms towards each other is quite different in both classes of compounds. In the very large rings where all atoms can move freely the ring compounds may follow the same formula as the straight chains do, but to the cases for which we now know the boiling points the value B 20,500 does not apply. We obtain satisfactory results however if we use $B=24{,}300$, as is demonstrated in Table VI.