159. *Boiling Point and Chemical Constitution. Part I. An Additive Function of Molecular Weight and Boiling Point.*

By V. C. E. Burnop.

The empirical quantity $M \log_{10}T + 8{\cdot}0\sqrt{M}$, denoted by (*b*), where *M* is the molecular weight and *T* the boiling point in degrees absolute, is shown to be additive. By examining the values of (*b*) for a number of compounds, the contributions to (*b*) of the separate atoms and structures within the molecule are found.

Various relations have been suggested between the boiling points of the members of homologous series and their molecular weights. Kopp (*Annalen*, 1842, **41**, 79, 86, 169) thought that the difference in boiling point between successive members of homologous series was always 19°, but Schorlemmer (*ibid.*, 1872, **161**, 281; 1878, **170**, 150; *Ber.*, 1871, **4**, 359, 564; 1874, **7**, 1131) showed that this rule was incorrect and that the CH_2 difference falls off continuously as molecular weight increases. Young (*Phil. Mag.*, 1905, **9**, 1) found that the difference *D* between the boiling point *T* of any compound and that of the next higher homologue is given by $D = 144{\cdot}86/T^{0{\cdot}0148\sqrt{T}}$. Walker (J., 1894, **65**, 193) put forward the expression $T = aM^b$, where *T* is the absolute boiling point, *M* the molecular weight, and *a* and *b* constants for a given homologous series. Boggio-Lera (*Gazzetta*, 1899, **29**, i, 441) modified this to the form $T = a\sqrt{M + b}$. Ramage used $T = aM\,(1 - 2^{-n})^{\frac{1}{2}}$, where *n* is the number of carbon atoms in the molecule. These expressions were applied to non-associated liquids. They relate boiling point and molecular weight, but are not otherwise concerned with molecular structure.

It is proposed to show that the expression $M \log_{10}T + 8{\cdot}0\sqrt{M}$, where *T* is the absolute boiling point at atmospheric pressure and *M* the molecular weight, is additive. The value of this function for any compound will be denoted by (*b*), this symbol also being used for the atomic and structural values.

From the values of (*b*) calculated for various homologous series, the following atomic and structural values have been obtained :

C	23·2	F	68	O	51·0	Br	255	Double bond	16·1
H	10·9	Cl	121·0	N	39·7	I	398	Triple bond	33·0
								Six-membered ring	17·6

Values of (*b*) derived from the observed boiling point are compared below with those calculated according to the figures just given.

Normal Paraffins, C_nH_{2n+2}; $(b) = 21{\cdot}8 + 45{\cdot}03n$.

n.	(*b*), obs.	(*b*), calc.	*n*.	(*b*), obs.	(*b*), calc.	*n*.	(*b*), obs.	(*b*), calc.
1	64·8	66·8	7	337·3	337·0	13	606·8	607·2
2	112·0	111·9	8	382·1	382·0	14	652·1	652·2
3	156·9	156·9	9	427·1	427·1	15	696·9	697·3
4	202·3	201·9	10	472·0	472·1	16	742·3	742·3
5	247·3	247·0	11	517·0	517·1	17	787·4	787·3
6	292·1	292·0	12	561·8	562·2	18	832·3	832·4

A branched-chain compound has a lower boiling point than the corresponding straight-chain compound :

Pentanes.

	T.	(*b*), obs.	Decrease.
$CH_2Me{\cdot}CH_2{\cdot}CH_2Me$	309°	247·3	—
$CHMe_2{\cdot}CH_2Me$	301	246·4	0·9
CMe_4	283	244·6	2·7

Hexanes.

	T.	(*b*), obs.	Decrease.
$CH_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Me$	342°	292·1	—
$CHMe(CH_2Me)_2$	337	291·8	0·3
$CH_2Me{\cdot}CH_2{\cdot}CHMe_2$	335	291·5	0·6
$CHMe_2{\cdot}CHMe_2$	331	291·0	1·1
$CH_2Me{\cdot}CMe_3$	322	290·0	2·1

Also, a β-methyl group causes a decrease in (*b*) of about 0·9.

	(*b*), obs.		
	n.	*iso*.	Diff.
Butane	202·3	201·4	0·9
Pentane	247·3	246·4	0·9
Hexane	292·1	291·5	0·6

	(*b*), obs.		
	n.	*iso*.	Diff.
Heptane	337·3	336·2	1·1
Octane	382·1	381·1	1·0

Unsaturated Hydrocarbons.—For the olefins, the calculated values of (*b*) agree very closely with those derived from observation. Among isomers, that with the double bond in the αβ-position has the lowest b. p. For those compounds in the table the mean values are: for an αβ-double bond, 16·0; for a βγ-double bond, 16·4; for a γδ-double bond, 16·3. A similar feature is noticed with the acetylenes: for an αβ-triple bond, 32·5; for a βγ-triple bond, 34·0. With the diolefins, the b. p. decreases as the number of carbon atoms between the double bond increases:

No. of C atoms between bonds	1	2	3
(*b*) for the double bond	16·7	16·4	15·7

Olefin.	(*b*), obs.	(*b*), calc.	Olefin.	(*b*), obs.	(*b*), calc.
$CH_2{:}CH_2$	104·6	106·1	$CH_2Me\cdot CH{:}CH\cdot CH_2Me$	286·5	286·1
$CH_2{:}CHMe$	150·8	151·1	$CH_2{:}CH\cdot[CH_2]_4\cdot CH_3$	330·9	331·1
$CH_2{:}CH\cdot CH_2Me$	196·1	196·1	$CHMe{:}CH\cdot[CH_2]_3\cdot CH_3$	331·2	,,
$CHMe{:}CHMe$	196·8	,,	$CH_2Me\cdot CH{:}CH\cdot[CH_2]_2\cdot CH_3$	331·1	,,
$CH_2{:}CH\cdot[CH_2]_2\cdot CH_3$	241·9	241·1	$CH_2{:}CH\cdot[CH_2]_5\cdot CH_3$	375·8	376·1
$CHMe{:}CH\cdot CH_2Me$	241·6	,,	$CH_2{:}CH\cdot[CH_2]_6\cdot CH_3$	421·0	421·1
$CH_2{:}CH\cdot[CH_2]_3\cdot CH_3$	285·8	286·1	$CH_2{:}CH\cdot[CH_2]_7\cdot CH_3$	465·7	466·1
$CHMe{:}CH\cdot[CH_2]_2\cdot CH_3$	286·2	,,			

Diolefin.	(*b*), obs.	(*b*), calc.	Diolefin.	(*b*), obs.	(*b*), calc.
$CH_2{:}C{:}CH_2$	146·1	145·4	$CH_2{:}CH\cdot CH_2\cdot CH{:}CH_2$	234·5	235·4
$CH_2{:}C{:}CHMe$	192·0	190·4	$CHMe{:}C{:}CHMe$	236·6	,,
$CH_2{:}CH\cdot CH{:}CH_2$	190·2	,,	$CH_2{:}CH\cdot[CH_2]_2\cdot CH{:}CH_2$	279·3	280·4
$CH_2{:}CH\cdot CH{:}CHMe$	236·0	235·4	$CHMe{:}CH\cdot CH{:}CHMe$	281·6	,,
$CH_2{:}C{:}CH\cdot CH_2Me$	236·3	,,			

Acetylene.	(*b*), obs.	(*b*), calc.	Acetylene.	(*b*), obs.	(*b*), calc.
$CH{\vdots}CH$	99·7	101·2	$CH{\vdots}C\cdot[CH_2]_3\cdot CH_3$	280·5	281·2
$CH{\vdots}CMe$	146·6	146·2	$CMe{\vdots}C\cdot[CH_2]_2\cdot CH_3$	281·8	,,
$CH{\vdots}C\cdot CH_2Me$	191·9	191·2	$CH{\vdots}C\cdot[CH_2]_4\cdot CH_3$	325·4	326·2
$CMe{\vdots}CMe$	192·9	,,	$CMe{\vdots}C\cdot[CH_2]_3\cdot CH_3$	326·8	,,
$CH{\vdots}C\cdot CH_2\cdot CH_2Me$	235·8	236·2	$CH{\vdots}C\cdot[CH_2]_5\cdot CH_3$	370·2	371·2
$CMe{\vdots}C\cdot CH_2Me$	237·3	,,	$CH{\vdots}C\cdot[CH_2]_6\cdot CH_3$	415·1	416·2

cyclo*Paraffins.*—The presence of a ring causes an increase in (*b*) of the same order as that due to a double bond.

Hydrocarbon.	(*b*), obs.	(*b*) for ring.	Hydrocarbon.	(*b*), obs.	(*b*) for ring.
*cyclo*Propane	151·0	16·0	Methyl*cyclo*hexane	332·3	17·3
*cyclo*Butane	197·7	17·7	*cyclo*Heptane	333·4	18·4
*cyclo*Pentane	242·8	17·8	*cyclo*Octane	378·5	18·5
*cyclo*Hexane	287·6	17·6	*cyclo*Nonane	423·7	18·7

Aromatic Hydrocarbons.—The value of (*b*) calculated for the Kekulé formula for benzene agrees well with the value derived from the b. p. Thus: $C_6 = 139{\cdot}2$, $H_6 = 65{\cdot}4$, three double bonds = 48·3, six-membered ring = 17·6, giving (*b*), calc. = 270·5. The observed value is 269·6.

Hydrocarbon.	(*b*), obs.	(*b*), calc.	Hydrocarbon.	(*b*), obs.	(*b*), calc.
Benzene	269·6	270·5	Propylbenzene	404·0	405·5
Toluene	314·3	315·5	Butylbenzene	448·9	450·5
Ethylbenzene	359·3	360·5	Amylbenzene	493·8	495·5

The transition from *cyclo*hexane to benzene is shown in the following table:

	(*b*), obs.	(*b*), calc.		(*b*), obs.	(*b*), calc.
*cyclo*Hexane	287·6	(287·6)	*cyclo*Hexa-1 : 4-diene	276·1	276·2
*cyclo*Hexene	282·0	281·9	Benzene	269·6	270·5
*cyclo*Hexa-1 : 3-diene	275·5	276·2			

Where two rings are fused together, each ring exerts its separate value of (*b*), as in the following table:

Hydrocarbon.	Rings.	Double bonds.	(*b*), obs.	(*b*), calc.
Naphthalene, $C_{10}H_8$	2	5	435·2	434·9
Tetrahydronaphthalene, $C_{10}H_{12}$	2	3	462·3	463·4
Decahydronaphthalene, $C_{10}H_{18}$	2	0	451·9	454·8
Anthracene, $C_{14}H_{10}$	3	7	604·8	599·3

The Halogens.—The following figures are obtained for the halogens at their b. p.'s, together with those for the hydrogen halides.

Halogen.	*(b)*, obs.	*(b)*, calc.	Hydrogen halide.	*(b)*, obs.	*(b)*, calc.
F_2	141·8	136	HCl	131·5	131·9
Cl_2	236·2	242	HBr	254·2	266
Br_2	504·2	510	HI	394·5	409
I_2	802·3	796			

Alkyl Chlorides, $C_nH_{2n+1}Cl$.—Values for the α- and β-chloro-*n*-paraffins are here compared with the values calculated from a mean figure for Cl. The b. p.'s of the β-chloroparaffins are lower than those of the α-compounds, causing a difference of about 1·5 in *(b)* between isomers in the two series.

n.	*(b)*, obs., α-chloro.	*(b)*, obs., β-chloro.	*(b)*, calc.	*n.*	*(b)*, obs., α-chloro.	*(b)*, obs., β-chloro.	*(b)*, calc.
1	178·0	—	176·9	5	357·5	356·1	356·9
2	222·7	—	221·9	6	402·2	401·0	401·9
3	267·7	266·4	266·9	7	447·6	446·0	446·9
4	312·4	311·3	311·9	8	493·0	491·1	491·9

n-*Alkyl bromides*, $C_nH_{2n+1}Br$.

n.	*(b)*, obs.	*(b)*, calc.	*n.*	*(b)*, obs.	*(b)*, calc.
1	310·5	311	5	491·5	491
2	355·1	356	6	537·0	536
3	400·7	401	7	582·2	581
4	446·2	446	8	628·1	626

n-*Alkyl iodides*, $C_nH_{2n+1}I$.

n.	*(b)*, obs.	*(b)*, calc.	*n.*	*(b)*, obs.	*(b)*, calc.
1	449·9	454	5	634·0	634
2	494·8	499	6	679·2	679
3	541·8	544	7	725·7	724
4	588·2	589	8	771·7	769

Halogenobenzenes.

	(b), obs.	*(b)*, calc.		*(b)*, obs.	*(b)*, calc.
Fluorobenzene	323·8	327·6	Bromobenzene	516·1	514·6
Chlorobenzene	378·0	380·6	Iodobenzene	657·9	657·6

Ethers and Esters.—These yield good results, *(b)*, calc. being very near *(b)*, obs. Among isomers that with the lowest b. p. is that in which the two groups R and R′ are the same, or differ only by CH_2. In the tables all the alkyl groups are normal. The double bond in the carbonyl group of the esters has the same value of *(b)* as in the olefins.

Ether.	*(b)*, obs.	*(b)*, calc.	Ether.	*(b)*, obs.	*(b)*, calc.	Ether.	*(b)*, obs.	*(b)*, calc.
Dimethyl	164·7	162·8	Methyl heptyl	433·0	432·8	Dioctyl	791·0	792·8
Methyl ethyl	209·1	207·8	Ethyl hexyl	431·2	,,	Benzyl ethyl	455·4	455·2
Diethyl	253·3	252·8	Dibutyl	431·8	,,	Phenyl methyl	367·6	365·2
Methyl butyl	298·5	297·8	Ethyl heptyl	477·1	477·8	Phenyl ethyl	412·4	410·2
Methyl amyl	341·8	342·8	Ethyl octyl	521·3	522·8	Phenyl propyl	456·1	458·2
Ethyl butyl	342·2	,,	Diamyl	522·4	,,	Phenyl hexyl	590·5	590·2
Dipropyl	342·1	,,	Dihexyl	612·1	612·8	Diphenyl	567·8	570·8
Ethyl amyl	387·4	387·8	Diheptyl	701·1	702·8			

Ester.	*(b)*, obs.	*(b)*, calc.	Ester.	*(b)*, obs.	*(b)*, calc.	Ester.	*(b)*, obs.	*(b)*, calc.
Methyl formate	211·1	208·1	Methyl valerate	388·5	388·1	Amyl acetate	432·6	433·1
Methyl acetate	255·5	253·1	Ethyl butyrate	387·7	,,	Hexyl formate	433·4	,,
Ethyl formate	255·2	,,	Propyl propionate	387·9	,,	Methyl heptoate	477·7	478·1
Methyl propionate	299·4	298·1	Butyl acetate	388·4	,,	Ethyl hexoate	477·0	,,
Ethyl acetate	299·2	,,	Amyl formate	388·9	,,	Propyl valerate	477·2	,,
Propyl formate	299·5	,,	Methyl hexoate	432·8	433·1	Butyl butyrate	477·0	,,
Methyl butyrate	343·6	343·1	Ethyl valerate	432·2	,,	Amyl propionate	476·8	,,
Ethyl propionate	343·2	,,	Propyl butyrate	431·8	,,	Hexyl acetate	477·5	,,
Propyl acetate	343·5	,,	Butyl propionate	432·2	,,	Heptyl formate	478·3	,,
Butyl formate	344·1	,,						

Aromatic esters.

	(b), obs.	*(b)*, calc.		*(b)*, obs.	*(b)*, calc.
Methyl benzoate	457·2	455·5	Benzyl acetate	501·4	500·5
Ethyl benzoate	501·1	500·5	Phenyl benzoate	661·2	660·5

Ketones.—With the value of *(b)* already found for the double bond from the olefins, the values of *(b)*, obs. for the aliphatic ketones are 2·9 units lower than the calculated. The differences amount to only 0·5—1·5% of the whole, but the constancy is remarkable. On the other hand, the aromatic ketones have values of (*b*) higher than the calculated.

Ketone.	(*b*), obs.	(*b*), calc.	Diff.	Ketone.	(*b*), obs.	(*b*), calc.	Diff.
Dimethyl	199·2	202·1	2·9	Ethyl hexyl	469·5	472·1	2·6
Methyl ethyl	244·3	247·1	2·8	„ heptyl	514·5	517·1	2·6
„ propyl	289·5	292·1	2·6	„ octyl	558·7	562·1	3·4
„ butyl	334·4	337·1	2·7	Dipropyl	378·9	387·1	3·2
„ amyl	379·6	382·1	2·5	Dibutyl	468·8	472·1	3·3
„ hexyl	424·8	427·1	2·3	Diamyl	559·2	562·1	2·9
„ heptyl	469·0	472·1	3·1				
„ octyl	514·8	517·1	2·3	Phenyl methyl	408·0	405·8	2·2
„ nonyl	559·5	562·1	2·6	„ ethyl	453·6	450·8	2·8
Diethyl	289·2	292·1	2·9	Benzyl methyl	453·5	450·8	2·7
Ethyl propyl	334·1	337·1	3·0	„ ethyl	497·5	495·8	1·7
„ butyl	379·5	382·1	2·6	Diphenyl	610·9	609·5	1·4
„ amyl	424·1	427·1	3·0	Dibenzyl	700·2	699·5	0·7

Amines.—The value of (*b*) for nitrogen was obtained from the differences between the aromatic compounds and the corresponding heterocyclic compounds in which the CH group is replaced by the nitrogen atom :

Heterocyclic.	(*b*).	Aromatic.	(*b*).	Diff.	(*b*) for N.
Pyridine	275·7	Benzene	269·6	6·1	40·2
Quinoline	440·3	Naphthalene	435·2	5·1	39·2
Piperidine	293·1	*cyclo*Hexane	287·6	5·5	39·6

The mean value of 39·7 leads to good agreement between the values of (*b*) observed and calculated for the amines. Usually the former is 1—2 units high but this is possibly explained by association.

n-*Alkylamines*, $C_nH_{2n+1}\cdot NH_2$.

n.	(*b*), obs.	(*b*), calc.	*n*.	(*b*), obs.	(*b*), calc.	*n*.	(*b*), obs.	(*b*), calc.
1	119·7	117·4	6	343·7	342·4	10	523·4	522·4
2	163·7	162·4	7	388·8	387·4	11	567·7	567·4
3	209·9	207·4	8	433·8	432·4	12	612·5	612·4
4	254·3	252·4	9	478·7	477·4	13	657·0	657·4
5	298·9	297·4						

Other amines.

	(*b*), obs.	(*b*), calc.		(*b*), obs.	(*b*), calc.		(*b*), obs.	(*b*), calc.
NH_3	73·4	72·4	NEt_3	339·0	342·4	NHMePh ...	368·8	366·1
$NH_2\cdot NH_2$ ...	128·2	123·0	NH_2Ph	324·8	321·1	NMe_2Ph	411·0	411·1
$NHMe_2$	164·0	163·7	$NHPh_2$	570·8	569·8	NHEtPh ...	411·6	411·1
NMe_3	206·8	207·4	NPh_3	813·0	815·9	NEt_2Ph	498·7	501·1
$NHEt_2$	252·4	252·4						

The compounds dealt with in this paper (hydrocarbons, alkyl halides, ethers, esters, ketones, and amines) show clearly that the function (*b*) is additive. Associated compounds, such as the alcohols and the acids, have values of (*b*) higher than calculated, and it is proposed to treat them separately in a further paper.

IMPERIAL COLLEGE, LONDON, S.W. 7.

[*Received, April 28th*, 1938.]