

306. *Boiling Point and Chemical Constitution. Part II. A Method of calculating the Degree of Association at the Boiling Point.*

By V. C. E. BURNOP.

In Part I it was shown that the function $(b) = M \log T + 8.0\sqrt{M}$, where T is the absolute boiling point and M is the molecular weight, is additive for unassociated compounds, and the contributions to (b) of various atoms and structures were evaluated.

This function is now used to calculate the boiling point, T' , which an associated compound should have in the unassociated state; and, following Walker's generalisation that the molecular weights of related compounds vary approximately as the squares of their absolute boiling points, $(T/T')^2$ is regarded as giving the degree of association. These values are recorded for several classes of compound.

In Part I (this vol., p. 826) the quantity $(b) = M \log T + 8.0\sqrt{M}$, where M is the molecular weight and T the absolute boiling point, was shown to be additive for non-associated compounds. Since association results in a high boiling point, the value of (b) calculated for an associated liquid from the observed boiling point, *i.e.*, (b) , obs., is much higher than that calculated for a normal constitution, (b) , calc. Differences of nearly 10 units are found, in contrast to 1—2 units for non-associated compounds.

Methods of calculating the degree of association depend on the use of equations connecting molecular weight and physical properties, but different methods give discordant results (see Turner, "Molecular Association"). Ramsay and Shields (J., 1893, 63, 1089) introduced a factor α into their equation for molecular surface energy, and solution of $\gamma(M\alpha v)^{\frac{2}{3}} = k(T_0 - T - 6)$ for α gave the degree of association. Since surface tension is a surface property only, α does not represent the condition of the bulk of the liquid. The method about to be described, however, gives results in fair agreement with those of Ramsay and Shields.

The absolute boiling point, T' , which an unassociated compound of known constitution should have may be calculated by means of the formula $M \log T' + 8.0\sqrt{M} = (b)$, calc., and if the compound is associated, $T > T'$. Walker (J., 1894, 65, 193) has shown that the molecular weights of related compounds vary approximately as the squares of their absolute boiling points, so $(T/T')^2$ should give an estimate of the degree of association. The table on p. 1615 compares values of $(T/T')^2$ with the values of α given by Ramsay and Shields for temperatures at or near the boiling points.

Hydrogen fluoride is of special interest. The values of (b) for methyl, ethyl, and propyl fluorides are 124.6, 169.8, 214.4, giving for F the values 68.7, 68.9, 68.5; mean 68.7. Assuming that (b) , calc., for hydrogen fluoride is 79.6, we obtain $T' = 157^\circ$. The observed boiling point is 292°K. , hence the degree of association is 3.46. The vapour

density indicates degrees of association of 2.56 and 1.99, respectively, 7° and 12.6° above the boiling point, and on extrapolation these give 3.3 at the boiling point.

Compound.	$(T/T')^2$.	α .	Compound.	$(T/T')^2$.	α .
Methyl alcohol	3.34	3.24	Allyl alcohol	1.85	1.86
Ethyl "	2.40	2.43	Formic acid	2.62	3.13
Propyl "	1.91	2.31	Acetic "	2.07	2.77
isoPropyl "	1.75	2.72	Propionic "	1.81	1.88
Butyl "	1.68	1.76	Butyric "	1.64	1.69
isoButyl "	1.59	1.64	Valeric "	1.53	1.48
Amyl "	1.49	1.57	Propionitrile	1.45	1.57

For water, T' is 144° K. (−129°), leading to a value of 6.7 for the degree of association at 100°. Other methods give a lower figure; *e.g.*, Ramsay and Shields give 2.66, and Longinescu 4.7. Water is undoubtedly more associated than the alcohols, since it has a higher dipole moment (1.85; *cf.* 1.64 for MeOH, 1.58 for EtOH), and the poles are not sheltered: the alkyl groups of the alcohols reduce intermolecular forces by screening the hydroxyl group, but in water the two hydrogen atoms afford no shelter. All methods of determination being considered, the degrees of association at the boiling point of methyl and ethyl alcohols are about 3 and 2 respectively, which indicate that for water a value of at least 4 is to be expected.

The degrees of association at the boiling point of some alcohols, phenols, acids, amides, nitriles, and amines are given below: T is the observed absolute boiling point, and T' that calculated for the simple molecule.

n-Primary alcohols, C_nH_{2n+1}OH.

<i>n</i> .	(<i>b</i>), obs.	(<i>b</i>), calc.	<i>T</i> .	<i>T'</i> .	$(T/T')^2$.	<i>n</i> .	(<i>b</i>), obs.	(<i>b</i>), calc.	<i>T</i> .	<i>T'</i> .	$(T/T')^2$.
1	126.2	117.8	338°	185°	3.34	6	349.2	342.8	430°	370°	1.35
2	171.5	162.8	352	227	2.40	7	394.1	387.8	449	395	1.29
3	216.4	207.8	370	268	1.91	8	438.4	432.8	467	423	1.22
4	261.0	252.8	391	302	1.68	9	483.2	477.8	485	446	1.18
5	305.2	297.8	411	337	1.49	10	528.0	522.8	504	467	1.16

Secondary alcohols.

(1) C_nH_{2n+1}·CHMe·OH.

1	215.2	207.8	355	268	1.75	5	392.5	387.8	434	395	1.21
2	259.5	252.8	373	302	1.53	6	436.5	432.8	452	423	1.15
3	303.6	297.8	392	337	1.35	7	481.3	477.8	471	446	1.11
4	347.8	342.8	413	370	1.25						

(2) C_nH_{2n+1}·CHEt·OH.

2	303.1	297.8	388	337	1.33	4	391.9	387.8	429	395	1.18
3	347.3	342.8	408	370	1.22						

Tertiary alcohols.

Alcohol.	(<i>b</i>), obs.	(<i>b</i>), calc.	<i>T</i> .	<i>T'</i> .	$(T/T')^2$.
CMe ₃ ·OH	258.0	252.8	356°	302°	1.39
CEt ₃ ·OH	390.0	387.8	414	395	1.10
CPe ₃ ·OH	522.5	522.8	464	467	0.99

Among isomeric alcohols, the primary has the highest and the tertiary the lowest degree of association. Alcohols containing one double bond are slightly less associated than the corresponding saturated compounds, and cyclic alcohols have approximately the same degree of association as the straight-chain secondary alcohols with the same number of carbon atoms.

Butyl alcohols : T' = 302°.

Alcohol.	<i>T</i> .	$(T/T')^2$.
CH ₂ Me·CH ₂ ·CH ₂ ·OH	391°	1.68
CHMe ₂ ·CH ₂ ·OH ...	381	1.59
CH ₂ Me·CHMe·OH	373	1.53
CMe ₃ ·OH	356	1.39

n-Hexanols : T' = 370°.

Alcohol.	<i>T</i> .	$(T/T')^2$.
1-Hexanol.....	430°	1.35
2- "	413	1.25
3- "	408	1.22

n-Heptanols : T' = 395°.

Alcohol.	<i>T</i> .	$(T/T')^2$.
1-Heptanol.....	449°	1.29
2- "	434	1.21
3- "	429	1.18
4- "	429	1.18

Unsaturated alcohols.

Alcohol.	(b), obs.	(b), calc.	T.	T'.	(T/T') ² .
CH ₂ :CH·CH ₂ ·OH	209·8	202·1	370°	272°	1·85
CHMe:CH·CH ₂ ·OH	254·8	247·1	391	306	1·64
CH ₂ :CH·CH ₂ ·CH ₂ ·OH	254·4	"	386	"	1·60
CH ₂ :CH·CHMe·OH	252·9	"	369	"	1·46
CH ₂ :CH·CH ₂ ·CH ₂ ·CH ₂ ·OH.....	299·4	292·1	414	340	1·48
CH ₂ :CH·CHEt·OH	297·0	"	387	"	1·30
CHMe:CH·CHMe·OH	296·8	"	385	"	1·29
CH ₂ :CH·CH ₂ ·CHMe·OH	297·1	"	389	"	1·31

Miscellaneous compounds.

Phenol	327·6	321·5	455	394	1·33
Benzyl alcohol	372·5	366·5	478	420	1·30
<i>o</i> -Cresol	371·4	"	465	"	1·23
<i>m</i> - "	372·2	"	476	"	1·28
<i>p</i> - "	372·0	"	475	"	1·28
<i>cyclo</i> Pentanol	299·4	293·8	413	356	1·34
<i>cyclo</i> Hexanol	344·1	338·6	435	383	1·29
<i>cyclo</i> Heptanol	389·1	384·4	458	417	1·21
Glycol	228·8	213·8	470	270	3·03
Glycerol	330·0	309·8	563	340	2·74

n-Fatty acids, C_nH_{2n+1}·CO₂H.

<i>n</i> .	(b), obs.	(b), calc.	T.	T'.	(T/T') ² .	<i>n</i> .	(b), obs.	(b), calc.	T.	T'.	(T/T') ² .
0	172·7	163·1	374°	231°	2·62	5	397·4	388·1	478°	397°	1·45
1	217·6	208·1	391	272	2·07	6	442·1	433·1	497	425	1·37
2	262·7	253·1	414	308	1·81	7	486·7	478·1	513	448	1·31
3	307·6	298·1	437	341	1·64	8	531·1	523·1	527	469	1·26
4	352·5	343·1	460	372	1·53	9	575·6	568·1	542	491	1·22

For the isomeric acids C₄H₉·CO₂H, (*b*), calc. is 343·1, *T'* is 372°, and the other data are :

Acid.	(b), obs.	T.	(T/T') ² .	Acid.	(b), obs.	T.	(T/T') ² .
CH ₂ Et·CH ₂ ·CO ₂ H ...	352·5	460°	1·53	CHMeEt·CO ₂ H	351·2	447°	1·43
CH ₂ Pr ^β ·CO ₂ H	352·1	456	1·50	CMe ₃ ·CO ₂ H.....	350·3	437	1·38

For benzoic acid, (*b*), obs. = 420·0, (*b*), calc. = 411·8, *T* = 522°, *T'* = 444°, giving (T/T')² = 1·38.

The Amides.—These compounds decompose to some extent when boiled under ordinary pressure, and the boiling points of the first four members of the aliphatic series are approximately the same, instead of rising regularly as with other homologous compounds. The degrees of association are high; (*b*), calc. is for R·CO·NH₂.

Amide.	(b), obs.	(b), calc.	T.	T'.	(T/T') ² .
H·CO·NH ₂	174·6	162·7	484°	262°	3·40
CH ₃ ·CO·NH ₂	220·6	207·7	495	300	2·73
C ₂ H ₅ ·CO·NH ₂	264·8	252·7	486	333	2·34
C ₃ H ₇ ·CO·NH ₂	308·7	297·7	489	366	1·79

The Nitriles, C_nH_{2n+1}·C:N.

<i>n</i> .	(b), obs.	(b), calc.	T.	T'.	(T/T') ² .	<i>n</i> .	(b), obs.	(b), calc.	T.	T'.	(T/T') ² .
1	155·8	151·3	355°	275°	1·66	7	424·7	421·3	478°	449°	1·12
2	200·7	196·3	370	308	1·45	8	469·5	466·3	498	472	1·11
3	245·4	241·3	391	339	1·32	9	514·5	511·3	517	493	1·09
4	290·1	286·3	414	372	1·24	HCN	108·5	106·3	299	248	1·46
5	335·0	331·3	436	399	1·17	PhCN	355·8	355·0	468	457	1·05
6	379·8	376·3	457	427	1·15						

The Primary Amines.—These are more associated than the secondary and tertiary compounds (see Part I), again owing to the sheltering of the polar parts in the latter.

Amine.	T.	T'.	(T/T') ² .	Amine.	T.	T'.	(T/T') ² .
Methylamine	267°	224°	1·42	Ammonia	240°	206°	1·36
Ethylamine	290	258	1·26	Aniline	457	417	1·20
Propylamine	322	294	1·20				

Some compounds containing the carbonyl group show peculiar abnormalities. The esters (see Part I) and the acid chlorides are normal, showing that (*b*) for the carbonyl group is the sum for carbon, oxygen, and the double bond. It was found (*ibid.*) that for aliphatic ketones (*b*) is 2.9 units lower than calculated, but for aromatic ketones it is too high; and the aldehydes are similar. Since compounds containing oxygen tend to become associated, the low values are the more remarkable.

Acetyl	268.1	267.2	Butyryl	356.6	357.2
Propionyl	312.7	312.2	Valeryl	401.5	402.2

The Aldehydes, C_nH_{2n+1}·CHO.

<i>n.</i>	(<i>b</i>), obs.	(<i>b</i>), calc.	Diff.	<i>n.</i>	(<i>b</i>), obs.	(<i>b</i>), calc.	Diff.
0	106.1	112.1	6.0	4	289.9	292.1	2.2
1	152.5	157.1	4.6	5	334.8	337.1	2.3
2	198.5	202.1	3.6	6	380.3	382.1	1.8
3	244.5	247.1	2.6	Ph·CHO	363.9	360.8	-3.1

The importance of the dipole moment in problems of intermolecular forces and the association of liquids has been stressed by Keesom, Debye, London, and others (*e.g.*, London, *Trans. Faraday Soc.*, 1937, **33**, 8). Wolf explains association as entirely due to dipoles (*Z. physikal. Chem.*, 1929, *B*, **2**, 39), the molecules being held together by electrostatic forces, but there is spectroscopic evidence for the presence of hydrogen bonds in associated liquids. The molecules may be brought together by electrostatic attraction, and the formation of the hydrogen bond then follows. Association is favoured by a large dipole together with small dimensions (water and hydrogen fluoride) and by the presence of unsheltered poles. Dipole moment alone has little effect on boiling point and association; the *cis*-form of a disubstituted ethylene, for instance, does not always boil at a higher temperature than the *trans*-form. The small variations in boiling point of isomeric ethers, esters, etc., correspond to variations in intermolecular forces and hence in the dipole moment, but the four alcohols derived from *n*-heptane have identical dipole moments, whereas their boiling points vary over 20°. Of the three disubstituted benzene derivatives, however, that with the highest dipole moment has the highest boiling point, and is presumably the most associated. Some of the points mentioned are illustrated by the following tables.

Compound.	B. p., °K.		Dipole moment, D.		Compound.	B. p., °K.		Dipole moment, D.	
	<i>cis</i> -.	<i>trans</i> -.	<i>cis</i> -.	<i>trans</i> -.		<i>cis</i> -.	<i>trans</i> -.	<i>cis</i> -.	<i>trans</i> -.
CHCl:CHCl ...	333	321	1.85	0	CHCl:CHBr ...	358	348	1.55	—
CHBr:CHBr ...	385	381	1.35	0	CHCl:CHI.....	386	390	1.27	0.57
CHI:CHI	461	464	0.75	0					

Compound.	B. p., °K.			Dipole moment, D.		
	<i>o</i> -.	<i>m</i> -.	<i>p</i> -.	<i>o</i> -.	<i>m</i> -.	<i>p</i> -.
Xylene	417	412	411	0.6	0.4	0.0
Tolyl methyl ether	444	450	450	1.0	1.2	1.2
Dichlorobenzene	455	445	446	2.3	1.5	0.0
Nitrotoluene	495	504	511	3.8	4.2	4.5
Dinitrobenzene	592	576	572	6.0	4.0	0.8
Toluidine	473	476	473	1.5	1.4	1.3
Chlorophenol	449	487	490	1.3	2.1	2.2

The boiling points and degrees of association of the disubstituted benzene compounds C₆H₄RX, where R is a non-associating group and X an associating group (OH, NH₂, or CO₂H), are readily explained. The degree of association is nearly the same for *m*- and *p*-compounds, but less for *o*-compounds, where R has more effect; R exerts its greatest effect when X is a carboxyl group. The influence of the size of R is seen in the small degrees of association of the *o*-chloro-, *o*-bromo-, and *o*-phenyl-phenols, and the more effective sheltering afforded by the *isopropyl* than by the *n*-propyl group is also apparent.

Substituted phenols, $C_6H_4(OH)R$.

R=	(b), obs.	(b), calc.	T.	T'.	(T/T') ² .	R=	(b), obs.	(b), calc.	T.	T'.	(T/T') ² .
<i>o</i> -Cl	431.4	431.6	449°	451°	1.00	<i>o</i> -Pr ^β	457.9	456.5	477°	465°	1.05
<i>m</i> -Cl	435.8	"	487	"	1.18	<i>m</i> -Pr ^β	—	"	—	"	—
<i>p</i> -Cl	436.2	"	490	"	1.19	<i>p</i> -Pr ^β	460.9	"	502	"	1.16
<i>o</i> -Br	566.9	565.6	467	459	1.03	<i>o</i> -Bu	504.1	501.5	508	487	1.08
<i>m</i> -Br	573.8	"	510	"	1.22	<i>m</i> -Bu	505.8	"	521	"	1.14
<i>p</i> -Br	574.0	"	511	"	1.22	<i>p</i> -Bu	505.8	"	521	"	1.14
<i>o</i> -Me	371.4	366.5	465	420	1.23	<i>o</i> -Ph	570.1	570.2	548	548	1.00
<i>m</i> -Me	372.2	"	476	"	1.28	<i>m</i> -Ph	574.0	"	575	"	1.10
<i>p</i> -Me	372.0	"	475	"	1.28	<i>p</i> -Ph	574.9	"	581	"	1.12
<i>o</i> -Et	415.7	411.5	480	443	1.18	<i>o</i> -OMe	422.7	417.5	478	434	1.21
<i>m</i> -Et	416.5	"	487	"	1.21	<i>m</i> -OMe	427.1	"	516	"	1.41
<i>p</i> -Et	417.1	"	492	"	1.24	<i>p</i> -OMe	427.2	"	517	"	1.42
<i>o</i> -Pr ^α	459.6	456.5	493	465	1.12						
<i>m</i> -Pr ^α	460.8	"	501	"	1.16						
<i>p</i> -Pr ^α	461.3	"	505	"	1.18						

Substituted anilines, $C_6H_4R \cdot NH_2$.

<i>o</i> -Me	369.1	366.1	473	443	1.09	<i>o</i> -Cl	432.3	431.2	482	473	1.04
<i>m</i> -Me	370.3	"	476	"	1.11	<i>m</i> -Cl	434.7	"	503	"	1.13
<i>p</i> -Me	369.1	"	473	"	1.09	<i>p</i> -Cl	434.8	"	504	"	1.13

Substituted benzoic acids, $C_6H_4R \cdot CO_2H$.

<i>o</i> -Me	464.2	456.8	532	469	1.29	<i>o</i> -Et	507.1	501.8	532	491	1.18
<i>m</i> -Me	464.7	"	536	"	1.31	<i>o</i> -Pr	551.4	546.8	546	511	1.14
<i>p</i> -Me	466.0	"	548	"	1.37	<i>o</i> -Ph	665.2	660.6	616	583	1.12

IMPERIAL COLLEGE, LONDON, S.W. 7.

[Received, August 6th, 1938.]