

XVI. *On the Relation between Boiling-point and Composition in Organic Compounds.*
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 University of Giessen. Communicated by Dr. A. W. HOFMANN.

Received March 20,—Read May 3, 1860.

THE researches which I beg, in the following pages, to submit to the Royal Society, embody the results obtained in the further development of an observation which I made a considerable number of years ago, and which, since that time, I had to defend against the objections of others, both by experimental inquiries of my own, and by the collection and discussion of facts elicited in the investigations of other observers. As far back as 1841* I pointed out that in analogous compounds the same difference of composition frequently involves the same difference in boiling-points. The assertion of the existence of this law-like relation between the chemical composition of substances and one of their most important physical properties, when first enunciated, met rather with the opposition than with the assent of chemists. In Germany especially it was contested by SCHRÖDER in his memoir “On the Molecular Volume of Chemical Compounds†.” These objections led me to collect additional evidence‡ in favour of my views, and to show more particularly that in very extensive series of compounds (alcohols $C_n H_{n+2} O_2$; acids $C_n H_n O_4$; compound ethers $C_n H_n O_4$, &c.) an elementary difference $x C_2 H_2$ is attended by a difference of $x \times 19^\circ C.$ in the boiling-points, and how this fact is intimately connected with other regularities exhibited by the boiling-points of organic compounds. Almost at the same period SCHRÖDER§ convinced himself that the relation I had pointed out obtains in most cases. He collected himself a considerable number of illustrations of the regularities I had traced, and showed that the relation in question is rendered more especially conspicuous if the compounds be expressed by formulæ representing equal vapour-volumes of the several substances. Some of the views, however, which were peculiar to SCHRÖDER have not gained the approbation of chemists. This physicist was inclined to consider the boiling-point of a substance as the most essential criterion of its proximate constituents, as the most trustworthy indicator of its molecular constitution. His views were chiefly based upon the assumption that the elementary difference $C_2 H_2$, when occurring in alcohols $C_n H_{n+2} O_2$, involved a difference of boiling-points other than that occasioned by the same elementary difference obtaining in acids $C_n H_n O_4$,

* Ann. der Chem. und Pharm. vol. xlix. pp. 71 and 169.

† Ueber die Molecular-Volume der Chemischen Verbindungen, 1843.

‡ Ann. der Chem. und Pharm. vol. l. p. 128.

§ Ueber die Siedhitze der Chemischen Verbindungen, 1844.

and that the isomeric compound ethers differed from one another in their boiling-points. An extensive series of boiling-point determinations* which I made of these isomeric ethers, proved that the latter assumption is not founded on facts. The exertions made by SCHRÖDER, GERHARDT, LÖWIG and others, in the hope of recognizing the influence of the constituent elements on the boiling-point of a compound, have also essentially remained without result †.

In France the existence of the relations between composition and boiling-point which I had observed, has been contested by I. PIERRE‡, who determined the boiling-points of many organic compounds, while engaged in an inquiry regarding their expansion. In England, lastly, W. A. MILLER§ has likewise called attention to the discrepancies between the boiling-points observed by PIERRE and those calculated on the supposed existence of the relations which I had indicated. I was, however, enabled|| to remove these apparent discrepancies by the first results obtained in a long series of experimental observations of my own, in which, at intervals and as material and opportunities presented themselves, I have continued up to the present day.

The existence of the relations between composition and boiling-point, such as it results from my original observations, has, notwithstanding these objections, been generally acknowledged. In many cases the recognition of these relations furnished important arguments in discussions regarding the true molecular value of organic compounds. Chemists have observed a vast number of new illustrations, and for several series, in which the individual terms differ from each other by a constant elementary difference, the corresponding difference of boiling-point has been carefully determined¶. Nevertheless, these relations, the important means of control which they afford in experimental inquiries, and the assistance which they are frequently capable of lending in the determination of the true chemical character of a new compound, have scarcely been sufficiently appreciated.

The rapid progress of organic chemistry has greatly expanded the material available for the discussion of boiling-points, and up to the latest date the stream of experimental inquiry, whilst confirming or correcting former observations, has furnished a rich supply of additional important facts. The time has arrived when a survey of the territory safely acquired may be taken, and when from the boundary lines reached we may fix the directions in which we have next to advance.

A collection of my researches on this subject in a connected form, permitting this survey, and showing the results which may be expected from their application, I now beg leave to submit to the Royal Society, hoping that their attention may not be with-

* Ann. der Chem. und Pharm. vol. lv. p. 166.

† In reviewing SCHRÖDER's memoir on this subject, I have pointed out the reasons which render the general solution of this problem almost hopeless.—Pogg. Ann. vol. lxxxi. p. 374.

‡ Thèse soutenue à la Faculté des Sciences à Paris (Annuaire de Chimie, par MILLON et REISET, 1846).

§ Quarterly Journal of the Chemical Society, vol. i. p. 363.

|| Ibid. vol. iii. p. 104.

¶ The careful manner in which A. H. CHURCH (Phil. Mag. [4] ix. 256) has determined the difference of the boiling-points for the series of hydrocarbons $C_n H_{n-6}$, deserves especially to be mentioned.

held from a field where our knowledge, emanating from earlier observations, but expanded and consolidated more than ever before by recent experimental evidence, has already gained a solid foundation.

It is especially with regard to organic compounds that constant relations between boiling-point and composition have been demonstrated. It often occurs that in the case of analogous compounds the same difference in the boiling-points corresponds to the same difference in the chemical formulæ, or that the differences in boiling-points and those in composition are proportional. In different series of analogous compounds the same differences of boiling-point may correspond to the same differences of composition, but this does not obtain in all series. The regularities exhibited by the boiling-points of organic compounds, and more especially the observation of the same difference of boiling-point corresponding to the same difference of composition, are limited to certain groups. In other groups, the same difference in the formulæ involves another difference in the boiling-points.

Among the earliest recognized regularities, comprising at the same time the largest number of compounds, are the following:—An alcohol $C_n H_{n+2} O_2$, which contains $x C_2 H_2$ more or less than another, boils at a temperature $x \times 19^\circ$ higher or lower. An acid $C_n H_n O_4$, boils at a temperature 40° higher than the alcohol $C_n H_{n+2} O_2$, the oxidation of which may give rise to the acid. A compound ether $C_n H_n O_4$, boils at a temperature 82° lower than the acid $C_n H_n O_4$ isomeric with it. If we start from the boiling-point of ethyl-alcohol $=78^\circ$, these three propositions enable us to calculate the boiling-points of a large number of organic substances, alcohols, acids, and compound ethers, represented by the above general formulæ, as given in the following Table:—

TABLE I.

Calculated boiling-points.					
Alcohols $C_n H_{n+2} O_2$.		Acids $C_n H_n O_4$.		Compound ethers $C_n H_n O_4$.	
$C_2 H_4 O_2$	59°	$C_2 H_2 O_4$	99°	$C_4 H_4 O_4$	36°
$C_4 H_6 O_2$	78	$C_4 H_4 O_4$	118	$C_6 H_6 O_4$	55
$C_6 H_8 O_2$	97	$C_6 H_6 O_4$	137	$C_8 H_8 O_4$	74
$C_8 H_{10} O_2$	116	$C_8 H_8 O_4$	156	$C_{10} H_{10} O_4$	93
$C_{10} H_{12} O_2$	135	$C_{10} H_{10} O_4$	175	$C_{12} H_{12} O_4$	112
$C_{12} H_{14} O_2$	154	$C_{12} H_{12} O_4$	194	$C_{14} H_{14} O_4$	131
$C_{14} H_{16} O_2$	173	$C_{14} H_{14} O_4$	213	$C_{16} H_{16} O_4$	150
$C_{16} H_{18} O_2$	192	$C_{16} H_{16} O_4$	232	$C_{18} H_{18} O_4$	169
$C_{18} H_{20} O_2$	211	$C_{18} H_{18} O_4$	251	$C_{20} H_{20} O_4$	188
$C_{20} H_{22} O_2$	230	$C_{20} H_{20} O_4$	270	$C_{22} H_{22} O_4$	207
$C_{22} H_{24} O_2$	249	$C_{22} H_{22} O_4$	289	$C_{24} H_{24} O_4$	226
$C_{24} H_{26} O_2$	268	$C_{24} H_{24} O_4$	308	$C_{26} H_{26} O_4$	245
$C_{26} H_{28} O_2$	287	$C_{26} H_{26} O_4$	327	$C_{28} H_{28} O_4$	264
$C_{28} H_{30} O_2$	306	$C_{28} H_{28} O_4$	346	$C_{30} H_{30} O_4$	283
$C_{30} H_{32} O_2$	325	$C_{30} H_{30} O_4$	365	$C_{32} H_{32} O_4$	302
$C_{32} H_{34} O_2$	344	$C_{32} H_{32} O_4$	384		

The degree of accuracy with which the numbers of this Table represent the boiling-points of the several substances, may be gathered from a comparison of these numbers

with the results of observation, due attention being paid at the same time to the marked discrepancies exhibited by the several results of observation obtained in determining the boiling-point of one and the same substance.

In the following Tables I give the calculated boiling-points of a number of compounds side by side with the results of several observers:—

TABLE II.

Alcohols $C_n H_{n+2} O_2$.		Calculated.	Observed boiling-point.
Methyl-alcohol	$C_2 H_4 O_2$	59	{ Kane, 60°; Delffs, 60°·5; Kopp, 65°; Pierre, 66°; Dumas and Péligot, 66°·5.
Ethyl-alcohol	$C_4 H_6 O_2$	78	{ Dumas and Boullay, 76°; Gay-Lussac, Pierre, Kopp, Delffs, Andrews, 78°.
Propyl-alcohol	$C_6 H_8 O_2$	97	Chancel, 96°.
Butyl-alcohol	$C_8 H_{10} O_2$	116	Wurtz, 109°.
Amyl-alcohol	$C_{10} H_{12} O_2$	135	{ Pasteur, 127°—129°; Cahours, Pierre, Kopp, Delffs, 132°; Rieckher, 135°.
Caproyl-alcohol	$C_{12} H_{14} O_2$	154	Faget, 148°—154°.
Enanthy-alcohol	$C_{14} H_{16} O_2$	173	Städeler, 177°—177°·5.
Cetyl-alcohol	$C_{32} H_{34} O_2$	344	Favre and Silbermann, 366°?

TABLE III.

Acids $C_n H_n O_4$.		Calculated.	Observed boiling-point.
Formic acid	$C_2 H_2 O_4$	99	{ Liebig, 99°; Bineau, Favre and Silbermann, 100°; Kopp, 105°.
Acetic acid.....	$C_4 H_4 O_4$	118	{ Delffs, 116°; Kopp, 117°; Sébille-Auger, 119°; Dumas, 120°.
Propionic acid	$C_6 H_6 O_4$	137	{ Dumas, Malaguti and Leblanc, about 140°; Lim- pricht, Kopp, 142°.
Butyric acid	$C_8 H_8 O_4$	156	{ Kopp, Delffs, 156°; Pierre, 163°; Pelouze and Gélis, about 164°.
Valeric acid	$C_{10} H_{10} O_4$	175	Dumas and Stas, Delffs, 175°; Kopp, 176°.
Caproic acid	$C_{12} H_{12} O_4$	194	{ Brazier and Gossleth, Wurtz, 198°; Fehling, 202°— 209°.
Enanthylic acid	$C_{14} H_{14} O_4$	213	Städeler, 218°.
Caprylic acid	$C_{16} H_{16} O_4$	232	Fehling, 236°; Perrot, 238°.
Pelargonic acid	$C_{18} H_{18} O_4$	251	Perrot, 255°; Cahours, 260°.

TABLE IV.

Compound ethers $C_n H_m O_4$.		Calculated.	Observed boiling-point.
Formate of Methyl	$C_4 H_4 O_4$	36	Kopp, Andrews, 33°; Liebig, 36°—38°.
Acetate of Methyl	$C_6 H_6 O_4$	55	{ Andrews, 55°; Kopp, 56°; Dumas and Péligot, 58°. Liebig, Delffs, 53°; Kopp, 55°; Löwig, 56°.
Formate of Ethyl			
Acetate of Ethyl	$C_8 H_8 O_4$	74	Dumas and Boullay, Pierre, Kopp, Delffs, 74°.
Butyrate of Methyl	$C_{10} H_{10} O_4$	93	{ Favre and Silbermann, Delffs, 93°; Kopp, 95°; Pierre, [102°. Berthelot, about 90°. Wurtz, about 100°.
Acetate of Propyl			
Formate of Butyl			
Propionate of Ethyl	$C_{12} H_{12} O_4$	112	{ Kopp, 96°—98°; Limpricht and Uslar, 101°. Kopp, 114°—115°. Pelouze, 110°; Delffs, 113°; Kopp, 115°; Pierre, 119°. Wurtz, 114°.
Valerate of Methyl			
Butyrate of Ethyl			
Acetate of Butyl			
Formate of Amyl	$C_{14} H_{14} O_4$	131	{ Delffs, 114°; Kopp, about 116°. Delffs, 132°; Otto, Kopp, Berthelot, 133°—134°. Berthelot, about 130°.
Valerate of Ethyl			
Butyrate of Propyl			
Acetate of Amyl	$C_{16} H_{16} O_4$	150	{ Cahours, 125°; Kopp, Delffs, 133°. Lerch, 120°; Fehling, 162°.
Caproate of Ethyl			
Propionate of Amyl	$C_{18} H_{18} O_4$	169	{ Wrightson, about 155°. Delffs, 173°—176°.
Butyrate of Amyl			
Valerate of Amyl	$C_{20} H_{20} O_4$	188	{ Kopp, 188°; Balard, about 196°. Dachauer, 191°—192°; Bouis, 193°.
Acetate of Capryl			
Pelargonate of Ethyl	$C_{22} H_{22} O_4$	207	{ Cahours, 216°—218°; Delffs, 224°. Brazier and Gossleth, 211°.
Caproate of Amyl			
Laurostearate of Ethyl	$C_{28} H_{28} O_4$	264	Görgey, 264°; Delffs, 269°.

There can be no doubt that if the boiling-points of other alcohols, acids, and ethers belonging to these series were correctly observed, they also would agree within a few degrees with those obtained by calculation.

The boiling-points given in Table I. are closely connected with those of other monatomic alcohols with two equivalents of oxygen, of other monobasic acids with four equivalents of oxygen, and of the ethers generated by these acids and alcohols. It is frequently observed that a compound of this kind, which, when compared with an analogous body of Table I., contains $x \times C$ more or less, boils at a temperature $x \times 14.5$ higher or lower, or (what amounts to the same thing) that it boils at a temperature $x \times 5^\circ$ lower or higher, accordingly as it contains $x \times H$ more or less.

Benzoic acid, $C_{14} H_6 O_4$, for example, contains 8C more than the acid $C_6 H_6 O_4$, the boiling-point of which is stated in Table I. at 137°. Consequently the boiling-point of benzoic acid will be $137 + 8 \times 14.5 = 253$. It contains 8H less than the acid $C_{14} H_{14} O_4$, for the boiling-point of which the Table gives 213, and its boiling-point by calculation will be $213 + 8 \times 5 = 253$.

Allyl-alcohol, $C_6 H_8 O_2$, contains 2C more than ethyl-alcohol, $C_4 H_8 O_2$, which boils at 78°; the calculated boiling-point of allyl-alcohol accordingly is $78 + 2 \times 14.5 = 107$; or it may be compared to the alcohol $C_6 H_8 O_2$, the boiling-point of which is 97° (see Table I.), when the boiling-point of allyl-alcohol, which contains 2H less, will be found by calculation $= 107 (= 97 + 2 \times 5)$.

The following synopsis shows in how large a number of alcohols $C_n H_m O_2$, of acids and ethers $C_n H_m O_4$, the boiling-points obey this simple rule. In perusing this Table,

it must be borne in mind that the observations of boiling-points comprised in the higher ranges of the thermometer are frequently less accurate.

TABLE V.

Alcohols $C_n H_m O_2$.		Calculated.	Observed boiling-point.
Allyl-alcohol	$C_6 H_8 O_2$	107 ^o	Cahours and Hofmann, 103°.
Phenyl-alcohol	$C_{12} H_8 O_2$	194	Laurent, 187°—188°; Kopp, 188°.
Benzyl-alcohol	$C_{14} H_6 O_2$	213	Cannizzaro, 204°; Kopp, 207°.
Thymyl-alcohol.....	$C_{20} H_{14} O_2$	270	Kraut, 243°.
Styryl-alcohol	$C_{18} H_{10} O_2$	261	Wolff, 250°; E. Kopp, 254°.

TABLE VI.

Acids $C_n H_m O_4$.		Calculated.	Observed boiling-point.
Angelic acid	$C_{10} H_8 O_4$	185 ^o	Meyer and Zenner, 190°; Reinsch, 191°.
Pyroterebic acid	$C_{12} H_{10} O_4$	204	Rabourdin, 200°; Chautard, 210°.
Benzoic acid	$C_{14} H_6 O_4$	253	Kopp, 250°.
Terebenthilic acid.....	$C_{16} H_{10} O_4$	262	Personne, 250°.
Cinnamic acid	$C_{18} H_8 O_4$	301	Dumas and Péligot, 293°; E. Kopp, 300°—304°.
Toluic acid	$C_{16} H_8 O_4$	272	Strecker and Möller, 266°.

TABLE VII.

Compound ethers $C_n H_m O_4$.		Calculated.	Observed boiling-point.
Acetate of Allyl	$C_{10} H_8 O_4$	103 ^o	Cahours and Hofmann, 98°—100°; Zinin, 105°.
Butyrate of Allyl	$C_{14} H_{12} O_4$	141	Cahours and Hofmann, 140°; Berthelot, about 145°.
Valerate of Allyl.....	$C_{16} H_{14} O_4$	160	Cahours and Hofmann, 162°.
Acetate of Phenyl	$C_{16} H_8 O_4$	190	Scrugham, 188°.
Benzoate of Methyl			
Benzoate of Ethyl	$C_{18} H_{10} O_4$	209	Dumas and Péligot, Kopp, 199°.
Acetate of Benzyl			
Toluate of Ethyl.....	$C_{20} H_{12} O_4$	228	Delffs, 207°; Dumas and Boullay, 209°; Kopp, 213°; Cannizzaro, 210°.
Cuminate of Ethyl	$C_{24} H_{18} O_4$	266	Noad, 228°.
Benzoate of Amyl			
Enanthylate of Phenyl	$C_{26} H_{18} O_4$	285	Gerhardt and Cahours, 240°.
Benzoate of Allyl			
Cinnamate of Methyl	$C_{20} H_{10} O_4$	238	Rieckher, 252°—254°; Kopp, 261°.
Cinnamate of Ethyl	$C_{22} H_{12} O_4$	257	Cahours, 275°—280°.
Benzoate of Benzyl.....			
Caprylate of Phenyl	$C_{28} H_{20} O_4$	304	Berthelot and Luca, 230°; Zinin, 242°.
	$C_{28} H_{12} O_4$	344	E. Kopp, 241°.
	$C_{28} H_{20} O_4$	304	Marchand, 260°; E. Kopp, 262°; H. Kopp, 266°.
			Cannizzaro, 345°.
			Cahours, about 300°.

In all the series of analogous combinations quoted in the previous Tables, a compound containing in its formula $x C_2 H_2$ more than another is found to boil at a temperature $x \times 19^\circ$ higher. The same regularity obtains in other series of analogous compounds, but by no means in all. A few other groups may also be mentioned here, in which the observed boiling-points exhibit the above regularity, at all events within the limits of uncertainty usual in boiling-point determinations. The column containing the boiling-points calculated by means of the given rule is headed by the word "assumed."

TABLE VIII.

		Assumed.	Observed boiling-point.
Trichloracetate of Methyl	$C_6 Cl_3 H_3 O_4$	145°	Laurent, 145°.
Trichloracetate of Ethyl	$C_8 Cl_3 H_5 O_4$	164	Leblanc, 164°.
Nitrobenzoate of Methyl	$C_{16} H_7 N O_8$	279	Chancel, 279°.
Nitrobenzoate of Ethyl	$C_{18} H_9 N O_8$	298	E. Kopp, 296°; Chancel, 298°.
Xanthate of Methyl	$C_8 H_8 O_2 S_4$	180	Chancel, 179°.
Xanthate of Ethyl	$C_{10} H_{10} O_2 S_4$	199	Debus, 200°.
Nitrate of Methyl	$C_2 H_3 N O_6$	66	Dumas and Péligot, 86°.
Nitrate of Ethyl	$C_4 H_5 N O_6$	85	Millon, 85°; Kopp, 86°.
Nitrate of Butyl	$C_8 H_9 N O_6$	123	Wurtz, about 130°.
Nitrate of Amyl	$C_{10} H_{11} N O_6$	142	Rieckher, 137°; Hofmann, 148°.
Chloride of Acetyl	$C_4 H_3 O_2 Cl$	56	Gerhardt, 55°; Kopp, 55°—56°.
Chloride of Propionyl.....	$C_6 H_5 O_2 Cl$	75	Béchamp, about 80°.
Chloride of Butyryl	$C_8 H_7 O_2 Cl$	94	Gerhardt, 95°.
Chloride of Valeryl	$C_{10} H_9 O_2 Cl$	113	Béchamp, 115°—120°.
Dichloride of Ethylene	$C_4 H_4 Cl_2$	85	Dumas, 85°—86°; Pierre, 85°.
Dichloride of Propylene.....	$C_6 H_6 Cl_2$	104	Reynolds, 100°—103°; Cahours, 104°.
Dichloride of Butylene	$C_8 H_8 Cl_2$	123	Kopp, 122°; Kolbe, 123°.
Dichloride of C ₆ nanthylene	$C_{14} H_{14} Cl_2$	180	Limpricht, 187°.
Anisol (Phenate of Methyl)	$C_{14} H_9 O_3$	153	Cahours, 152°.
Phenetol (Phenate of Ethyl).....	$C_{16} H_{10} O_2$	172	Cahours, 172°; Baly, 175°.
Phenamyol (Phenate of Amyl)...	$C_{22} H_{16} O_2$	229	Cahours, 224°—225°.
Chloride of Benzoyl	$C_{14} H_5 O_2 Cl$	196	Malaguti, 195°; Cahours, 196°; Kopp, 198°.
Chloride of Toluyl	$C_{16} H_7 O_2 Cl$	215	Cahours, 214°—216°.
Hydride of Benzoyl	$C_{14} H_6 O_2$	179	Kopp, 179°.
Hydride of Cumyl	$C_{20} H_{12} O_2$	236	Gerhardt and Cahours, 220°; Kopp, 237°.

A few other series will be mentioned in a subsequent part of this paper. Since, as I have already remarked, the regularity in question is not altogether general, it may often be doubtful whether it exists or not when the observations of the boiling-points present considerable discrepancies and uncertainties in several terms of an homologous series. As an example, the following series may be quoted:—

TABLE IX.

		Assumed.	Observed boiling-point.
Cyanide of Methyl	$C_4 H_3 N$	79°	Kopp, 72°; Dumas, 77°; Buckton and Hofmann, 77°—78°.
Cyanide of Ethyl	$C_6 H_5 N$	98	Kolbe, Meyer, 88°; Grimm, Limpricht, 98°.
Cyanide of Propyl	$C_8 H_7 N$	117	Dumas, Malaguti and Leblanc, 118°·5
Cyanide of Butyl	$C_{10} H_9 N$	136	Schlieper, 125°; Guckelberger, 125°—128°.
Cyanide of Amyl	$C_{12} H_{11} N$	155	Frankland and Kolbe, 146°; Wurtz, 155°.

The comparison of the boiling-points of the corresponding terms in the several series of homologous substances given in the preceding Tables, exhibits several other constant differences in the boiling-points for certain differences in the formulæ. In addition

to those hitherto noticed, the following also deserve to be mentioned, since they are likewise observed in other compounds.

The foregoing Tables afford many illustrations of the facts, that the boiling-point of an acid lies 63° higher than that of the methyl-ether, 44° higher than that of the ethyl-ether, and 13° lower than that of the amyl-ether of the same acid. These regularities appear to obtain in the case of acids other than those quoted. The boiling-point of monochloroacetic acid (185° — 188° , R. HOFFMANN) has been found about 44° higher than that of the monochloroacetate of ethyl ($143^\circ\cdot5$, WILLM). Starting from the boiling-point of trichloroacetate of methyl (145° , LAURENT), or from that of trichloroacetate of ethyl (164° , LEBLANC), the boiling-point of trichloroacetic acid is found by calculation to be 208° . DUMAS found it between 195° and 200° . From the boiling-point of monobromoacetic acid, 208° , observed by PERKIN and DUPPA, that of the corresponding methyl-ether may be calculated at 145° , that of the ethyl-ether at 164° , and that of the amyl-ether at 221° . The results of observation are 144° , 159° , 207° . They are not, however, entirely to be relied upon, since the ethers of monobromoacetic acid, and especially those possessing higher boiling-points, are partially decomposed by ebullition.

In a few substances other than acids, the substitution of C_4H_5 for H is occasionally attended by a decrease of 44° in the boiling-point; that of C_2H_3 for H by a decrease of 63° . Ordinary (ethyl) ether, $C_8H_{10}O_2$, boils at 34° , *i. e.* 44° lower than ethyl-alcohol, $C_4H_6O_2$; methyl-amyl-ether, $C_{12}H_{14}O_2$, at 72° (WILLIAMSON), *i. e.* 63° lower than amyl-alcohol, $C_{10}H_{12}O_2$. If any doubt remained as to the expediency of representing ordinary ether by the formula $C_8H_{10}O_2 = (C_4H_5)(C_4H_5)O_2$, instead of the formula C_4H_5O , this observation might be of some importance; but the comparison of the boiling-points of alcohols and of so-called simple and mixed ethers, shows that the aforesaid regularity is not general, a circumstance arising from the fact of the elementary difference C_2H_2 , in the series of ethers $C_nH_{n+2}O_2$, involving a difference of boiling-points other than that corresponding to the elementary difference C_2H_2 in the series of alcohols $C_nH_{n+2}O_2$.

The preceding Tables contain a great number of illustrations of the facts, that many compounds containing benzoyl ($C_{14}H_5O_2$) or benzyl ($C_{14}H_7$) boil at a temperature 78° higher than the corresponding compounds of valeryl ($C_{10}H_9O_2$) or of amyl ($C_{10}H_{11}$). The benzoyl- and benzyl-compounds, when compared with the compounds of valeryl and amyl, contain 4C more and 4H less. They boil mostly, in accordance with the rules given (page 261), at a temperature $(4 \times 14^\circ\cdot5) + (4 \times 5^\circ) = 78^\circ$ higher.

In addition to the compounds, the boiling-points of which have already been given, the following exhibit the same regularity. [The mixed acetone A is the one obtained by the distillation of a mixture of an acetate and benzoate; the acetone B is that formed by distilling an acetate and valerate. Hydride of benzyl is identical with toluol, chloride of benzyl with monochlorinated toluol.]

TABLE X.

		Observed boiling-point.
Hydride of Benzoyl	$C_{14}H_6O_2$	Kopp, 179°.
Hydride of Valeryl.....	$C_{10}H_{10}O_2$	Kopp, 93°; Limpricht, 96°; Chancel, about 110°.
Chloride of Benzoyl	$C_{14}H_5O_2Cl$	Malaguti, 195°; Cahours, 196°; Kopp, 198°.
Chloride of Valeryl.....	$C_{10}H_9O_2Cl$	Béchamp, 115°—120°.
Mixed Acetone A	$C_{16}H_8O_2$	Friedel, 198°.
Mixed Acetone B	$C_{12}H_{12}O_2$	Williamson, 120°.
Hydride of Benzyl	$C_{14}H_2$	Church, 104°; Deville, 108°; Gerhardt, 114°.
Hydride of Amyl	$C_{10}H_{12}$	Frankland, 30°.
Chloride of Benzyl	$C_{14}H_7Cl$	Cannizzaro, 175°—176°.
Chloride of Amyl	$C_{10}H_{11}Cl$	Balard, Kopp, 101°; Pierre, Cahours, 102°.

This regularity does not, however, obtain in a general manner, as will be apparent by comparing the boiling-points of cyanide of phenyl (benzotrile, FEHLING, KOPP, 191°; LIMPRICHT, 192°) and of cyanide of butyl (valeronitrile, SCHLIEPER, 125°; GUCKELBERGER, from 125° to 128°), or the boiling-points of toluidine (MUSPRATT and HOFMANN, 198°) and of amylamine (BRAZIER and GOSSLETH, 93°; WURTZ, 95°).

The boiling-points of the terms of several series which have been previously mentioned frequently almost coincide, a circumstance which furnishes a valuable means of controlling boiling-point observations. If, for example, in a series of methyl-ethers, corresponding to various monobasic acids with four equivalents of oxygen, and in the chlorides of the radicals contained in the same acids, the boiling-points be found so near to each other as is shown in the following Table,—

TABLE XI.

		Observed boiling-point.
Acetate of Methyl	$C_8H_6O_4$	Andrews, 55°; Kopp, 56°; Dumas and Péligot, 58°.
Chloride of Acetyl.....	$C_4H_5O_2Cl$	Gerhardt, 55°; Kopp, 55°—56°.
Propionate of Methyl.....	$C_8H_8O_4$	Calculated, 74°.
Chloride of Propionyl	$C_6H_5O_2Cl$	Béchamp, about 80°.
Butyrate of Methyl	$C_{10}H_{10}O_4$	Favre and Silbermann, Delffs, 93°; Kopp, 95°; Pierre, 102°.
Chloride of Butyryl	$C_8H_7O_2Cl$	Gerhardt, 95°.
Valerate of Methyl.....	$C_{12}H_{12}O_4$	Kopp, 114°—115°.
Chloride of Valeryl	$C_{10}H_9O_2Cl$	Béchamp, 115°—120°.
Benzoate of Methyl	$C_{16}H_8O_4$	Dumas and Péligot, Kopp, 199°.
Chloride of Benzoyl	$C_{14}H_5O_2Cl$	Malaguti, 195°; Cahours, 196°; Kopp, 198°.
Toluate of Methyl.....	$C_{18}H_{10}O_4$	Calculated, 209°.
Chloride of Toluylyl.....	$C_{16}H_7O_2Cl$	Cahours, 214°—216°.

we are justified in expecting that new determinations will furnish also a more perfect coincidence of the boiling-points of the following pairs of substances:—

TABLE XII.

		Boiling-point.
Pelargonate of Methyl	$C_{20}H_{20}O_4$	Calculated, 188°.
Chloride of Pelargonyl	$C_{18}H_{17}O_2Cl$	Cahours, 220°.
Nitrobenzoate of Methyl ...	$C_{16}H_7(NO_4)O_4$	Chancel, 279°.
Chloride of Nitrobenzoyl ...	$C_{14}H_4(NO_4)O_2Cl$	Cahours, 265°—268°.
Cuminate of Methyl	$C_{22}H_{14}O_4$	Calculated, 247°.
Chloride of Cumyl	$C_{20}H_{11}O_2Cl$	Cahours, 258°—260°.
Cinnamate of Methyl	$C_{20}H_{10}O_4$	E. Kopp, 241°.
Chloride of Cinnamyl	$C_{18}H_7O_2Cl$	Cahours, 262°.

It is evident from the preceding Tables that phenyl-alcohol, acetate, cœnanthylate, and caprylate of phenyl boil at a temperature 116° higher than the corresponding ethyl-compounds (phenyl contains 8C more than ethyl, $8 \times 14^{\circ}5 = 116^{\circ}$). The same difference is not observed in all corresponding phenyl- and ethyl-compounds, yet it occurs in cases other than those already mentioned, or which may be readily inferred from the regularities previously alluded to. Thus the boiling-point of iodide of phenyl (SCRUGHAM, 190°) is likewise about 116° higher than that of iodide of ethyl (PIERRE, 70°; ANDREWS, 71°; FRANKLAND, 72°). It deserves also to be noticed that the boiling-points of acetate of phenyl (SCRUGHAM, 188°) and of iodide of phenyl (SCRUGHAM, 190°) are as near to each other as those of acetate of ethyl (74°) and of iodide of ethyl (70°—72°); and that the same difference is observed between the boiling-points of iodide of phenyl (190°) and of iodide of ethyl (70°—72°) as between those of chloride of phenyl (SCRUGHAM, 136°) and of chloride of ethyl (PIERRE, 11°; THÉNARD, 12°).

The compounds of allyl contain 2 C more in their formulæ than the corresponding ethyl-compounds. The difference in the boiling-points $2 \times 14^{\circ}5 = 29^{\circ}$ occurs not only in the compounds already quoted (the alcohols, acetates, butyrates, valerates, benzoates), but also approximately at least in the cyanates (cyanate of ethyl 60°, according to WURTZ; cyanate of allyl 82°, according to CAHOURS and HOFMANN); in the iodides (iodide of ethyl 70°, according to PIERRE; 72°, according to FRANKLAND; iodide of allyl 101°, according to BERTHELOT and LUCA); in the ethyl-ethers (ordinary ethyl-ether, $C_8H_{10}O_2$, 34°; allyl-ethyl-ether, $C_{10}H_{10}O_2$, 62°5, according to BERTHELOT and LUCA); and even in the aldehydes (acetic aldehyde, $C_4H_4O_2$, 20°, according to KOPP; 22°, according to LIEBIG and to PIERRE; acrolein, $C_6H_4O_2$, about 52°, according to REDTENBACHER). But in the case also of corresponding ethyl and allyl compounds, the difference in the boiling-points is by no means altogether constant, as is apparent from a comparison of the boiling-points of sulphocyanide of ethyl (146°, according to CAHOURS) and of sulphocyanide of allyl (143°, according to DUMAS and PELOUZE; 148°, according to WILL; 151°, according to KOPP).

If, on comparing the parallel terms of different series of compounds, we do not quite generally meet with the same difference in the boiling-points corresponding to the same

difference in composition, this fact arises from the circumstance that the same difference in the formulæ by no means involves the same difference of boiling-point in all series of homologous substances. For the series of the monatomic alcohols with two equivalents of oxygen, of the monobasic acids with four equivalents of oxygen, of the ethers to which both classes give rise, as well as for a few other series of homologous substances (see Table VIII.), the elementary difference $x C_2 H_2$ seems to involve a difference of boiling-point $x \times 19^\circ$; but there are other series of homologous bodies in which the same elementary difference is positively attended by another, greater or smaller, difference of boiling-point.

This difference is greater, for example, in the series of hydrocarbons $C_n H_{n-6}$, in which it amounts to about 24° .

TABLE XIII.

Benzol.....	$C_{12} H_6$	Kopp, 80° ; Mansfield, Church, 81° ; Faraday, Mitscherlich, 86° .
Toluol.....	$C_{14} H_8$	Church, 104° ; Deville, 108° ; Noad, 110° ; Gerhardt, 114° .
Xylol.....	$C_{16} H_{10}$	Church, 126° ; Cahours, 129° .
Cumol.....	$C_{18} H_{12}$	Abel, Church, 148° ; Gerhardt and Cahours, 151° .
Cymol.....	$C_{20} H_{14}$	Mansfield, Church, 171° ; Gerhardt and Cahours, 175° ; Kopp, 178° .

Nearly equally great is the difference in the isolated alcohol radicals $C_n H_{n+2}$.

TABLE XIV.

$C_{12} H_{14}$:—	Propyl, 68° (Williams); ethyl-butyl, 62° (Wurtz).
$C_{14} H_{16}$:—	Methyl-caproyl, 82° (Wurtz); ethyl-amyl, 88° (Wurtz).
$C_{16} H_{18}$:—	Butyl, 106° (Wurtz); 108° (Kolbe); 109° (Kopp).
$C_{18} H_{20}$:—	Butyl-amyl, 132° (Wurtz).
$C_{20} H_{22}$:—	Amyl, 155° (Frankland); 158° (Wurtz); butyl-caproyl, 155° (Wurtz).
$C_{24} H_{26}$:—	Caproyl (Brazier and Gossleth, Williams), 202° .

In the acetones and aldehydes $C_n H_n O_2$, the difference in the boiling-points corresponding to the elementary difference $C_2 H_2$ is likewise greater than 19° ; the boiling-points of several of the terms of these series are, however, but very imperfectly known. Those of the acetones seem to have been the more accurately determined.

TABLE XV.

Diff.				Diff.
$2 C_2 H_2$...	$C_6 H_6 O_2$...	Acetone	Liebig, Dumas, Kopp, 56°	2×22
$2 C_2 H_2$...	$C_{10} H_{10} O_2$...	Propione	Limpricht and Uslar, 110° ; Friedel, 111°	2×22
$6 C_2 H_2$...	$C_{14} H_{14} O_2$...	Butyrone	Chancel, about 144° ; Friedel, about 145°	6×20
	$C_{26} H_{26} O_2$...	Ænanthylone	Uslar and Seekamp, 264°	

The boiling-points of the so-called simple and mixed ethers $C_n H_{n+2} O_2$ also differ by more than 19° for $C_2 H_2$. But in this series also the boiling-points of but few terms have been accurately observed. The available data, some of which will claim our attention hereafter, are the following:—

TABLE XVI.

$C_4 H_8 O_2$:—Methyl-ether, Berthelot, -21° .
$C_6 H_{12} O_2$:—Methyl-ethyl-ether, Williamson, 11° .
$C_8 H_{16} O_2$:—Ethyl-ether, Dumas and Boullay, Kopp, 34° ; Andrews, Delffs, 35° .
$C_{12} H_{24} O_2$:—Methyl-amyl-ether, Williamson, 72° ; ethyl-butyl-ether, Wurtz, $78^\circ-80^\circ$.
$C_{14} H_{28} O_2$:—Ethyl-amyl-ether, Williamson, 112° ; Guthrie, $111^\circ-113^\circ$.
$C_{16} H_{32} O_2$:—Butyl-ether, Wurtz, $100^\circ-104^\circ?$
$C_{20} H_{40} O_2$:—Amyl-ether, Gaultier, 170° ; Wurtz, $170^\circ-175^\circ$; Rieckher, $175^\circ-183^\circ$.

Still greater (amounting to about 30°) is the difference in the boiling-points corresponding to the elementary difference $C_2 H_2$ in the chlorides, bromides, and iodides of the alcohol radicals, $C_n H_{n+1}$. The boiling-points of the methyl, ethyl, butyl, and amyl compounds are known with tolerable certainty.

TABLE XVII.

Diff.			Diff.
$C_2 H_2$	$C_2 H_3 Cl$	Berthelot, -20°	
$2 C_2 H_2$	$C_4 H_5 Cl$	Pierre, $+11^\circ$	31
$2 C_2 H_2$	$C_8 H_9 Cl$	Wurtz ($70^\circ-75^\circ$), 73°	2×31
$C_2 H_2$	$C_{10} H_{11} Cl$	Pierre, Cahours, 102°	29
$C_2 H_2$	$C_2 H_3 Br$...	Pierre, 13°	28
$2 C_2 H_2$	$C_4 H_5 Br$...	Pierre, 41°	2×24
$2 C_2 H_2$	$C_8 H_9 Br$...	Wurtz, 89°	2×30
$C_2 H_2$	$C_{10} H_{11} Br$...	Pierre, 119°	30
$C_2 H_2$	$C_2 H_3 I$	Andrews, 42° ; Pierre, 44°	27
$2 C_2 H_2$	$C_4 H_5 I$	Pierre, 70° ; Andrews, 71° ; Frankland, 72°	2×25
$2 C_2 H_2$	$C_8 H_9 I$	Wurtz, 121°	2×25
$C_2 H_2$	$C_{10} H_{11} I$	Frankland, 146° ; Kopp, 148° ; Grimm, 149°	28

Similar remarks apply to the sulphides $(C_n H_{n+1})_2 S_2$:

TABLE XVIII.

Diff.			Diff.
$2 C_2 H_2$	$C_4 H_6 S_2$	Regnault, 41°	2×25
$6 C_2 H_2$	$C_6 H_{10} S_2$	Pierre, 91°	6×21
	$C_{20} H_{22} S_2$	Balard, 216°	

Also to the Mercaptans $(C_n H_{n+1}) H S_2$.

$2 C_2 H_2$	$C_4 H_6 S_2$	Liebig, 36°	2×26
$C_2 H_2$	$C_6 H_{10} S_2$	Humann, 88°	$29-32$
	$C_{10} H_{12} S_2$	Krutzsch, 117° ; Kopp, 120°	

On the contrary, the difference in the boiling-points is less than 19° in the anhydrous acids (anhydrides) $C_n H_{n-2} O_6$.

TABLE XIX.

Diff.		Anhydrous.		Diff.
$2 C_2 H_2$	$C_8 H_6 O_6$	Acetic acid	Gerhardt, Kopp, 138°	$\dots\dots 2 \times 13.5$
$2 C_2 H_2$	$C_{12} H_{10} O_6$	Propionic acid	Limpricht and Uslar, 165°	$\dots\dots 2 \times 12.5$
$2 C_2 H_2$	$C_{16} H_{14} O_6$	Butyric acid	Gerhardt, about 190°	$\dots\dots 2 \times 12.5$
$6 C_2 H_2$	$C_{20} H_{18} O_6$	Valeric acid	Chiozza, about 215°	$\dots\dots 6 \times 12.5$
	$C_{32} H_{30} O_6$	Caprylic acid	Chiozza, about 290°	

In the ethers of the acids $C_n H_{n-2} O_8$, homologous to oxalic acid, the difference in boiling-point corresponding to the elementary difference $C_2 H_2$ seems to be about 14° ; this number, however, is somewhat uncertain, as boiling-points rather differing from one another have in some cases been observed for isomeric ethers. Isomeric with the latter, or belonging to the same series, are those ethers derived from the glycols $C_n H_{n+2} O_4$ by the action of two equivalents of an acid $C_n H_n O_4$. All the data respecting the boiling-points of these ethers, $C_n H_{n-2} O_8$, are collected in the following Table:—

TABLE XX.

$C_8 H_6 O_8$...	Oxalate of Methyl	Dumas and Péligot, 161° ; Delffs, 164° .
	Oxalate of Ethyl	Kopp, 185° ; Delffs, 186° .
$C_{12} H_{10} O_8$...	Succinate of Methyl	Fehling, 198° .
	Diacetate of Ethyl-glycol	Wurtz, 186° — 187° .
$C_{14} H_{12} O_8$...	Diacetate of Propyl-glycol	Wurtz, 186° .
	Succinate of Ethyl	D'Arcet, Fehling, 214° ; Kopp, 217° .
$C_{16} H_{14} O_8$...	Diacetate of Butyl-glycol	Wurtz, about 200° .
	Butyro-acetate of Ethyl-glycol ...	Simpson, 208° — 215° .
$C_{18} H_{16} O_8$...	Diacetate of Amyl-glycol	Wurtz, above 200° .
	Valer-acetate of Ethyl-glycol ...	Lourenço, about 230° .
$C_{20} H_{18} O_8$...	Dibutyrate of Ethyl-glycol	Wurtz, 239° — 241° .
	Suberate of Ethyl	Laurent, 260° .
$C_{24} H_{22} O_8$...	Oxalate of Amyl	Cahours, 260° ; Balard, 262° .
	Sebate of Methyl	Carlet, 285° .
	Divalerate of Ethyl-glycol	Lourenço, about 255° .
$C_{28} H_{26} O_8$...	Sebate of Ethyl	Carlet, 308° .

The difference is also less than 19° in the carbonates, the sulphocyanides, the borates of the alcohol radicals $C_n H_{n+1}$, and in the bromides of the diatomic radicals $C_n H_n$.

TABLE XXI.

Diff.			Diff.
$4 C_2 H_2$	$C_{10} H_{10} O_3$	Ettling, Cahours, 125°	$\dots\dots 4 \times 16$
$2 C_2 H_2$	$C_{18} H_{18} O_3$	Wurtz, 190°	$\dots\dots 2 \times 18$
	$C_{22} H_{22} O_3$	Medlock, 224° ; Bruce, 226°	
$C_2 H_2$	$C_4 H_3 N S_2$	Pierre, 133° ; Cahours, 132°	$\dots\dots 14$
$3 C_2 H_2$	$C_6 H_5 N S_2$	Cahours, 146°	$\dots\dots 3 \times 17$
	$C_{12} H_{11} N S_2$	Henry, 195° — 210° ; Medlock, 197°	
$3 C_2 H_2$	$3 C_2 H_3 O, B O_3$	Ebelmen and Bouquet, 72°	$\dots\dots 3 \times 16$
$9 C_2 H_2$	$3 C_4 H_5 O, B O_3$	Ebelmen and Bouquet, 119° ; Bowman, 121°	$\dots\dots 9 \times 17$
	$3 C_{10} H_{11} O, B O_3$	Ebelmen and Bouquet, 270° — 275°	
$C_2 H_2$	$C_4 H_4 Br_2$	Regnault, 129° ; Pierre, 133° ; Cahours, 130°	$\dots\dots 15$
$C_2 H_2$	$C_6 H_6 Br_2$	Reynolds, 143° ; Cahours, 145°	$\dots\dots 15$
	$C_8 H_8 Br_2$	Wurtz, about 158° ; Cahours, 160°	

There can be no doubt that in different series of homologous compounds the difference of boiling-point corresponding to the elementary difference $x \text{ C}_2 \text{ H}_2$ may vary; that frequently it is found to be $x \times 19^\circ$, but sometimes more, sometimes less. As to these inequalities of differences, they are sure to be governed by a more general law, which will probably be recognized when a sufficient number of boiling-points shall have been determined under a pressure different from the ordinary pressure of the atmosphere; for it cannot by any means be taken for granted that two substances will exhibit the same difference of boiling-point, whatever may be the pressure. Let S and S_1 be the boiling-points of two liquids under the ordinary pressure, and s and s_1 the boiling-points under another pressure. Then the assumption of $S - S_1 = s - s_1$ would involve the inference $S - s = S_1 - s_1$; *i. e.* that the boiling-points must undergo precisely the same change for the same change of pressure. But this conclusion, the so-called law of DALTON, is by no means correct; and it may be legitimately held that the homologous substances which under the ordinary pressure do not exhibit the most frequently observed difference of boiling-point (19°) for the elementary difference $\text{C}_2 \text{ H}_2$, would certainly show that difference under a different pressure.

Sufficient data are still wanting for the appreciation of the mode in which differences in boiling-points are affected by changes of pressure. But the extent of these alterations may in a measure be inferred from the fact that the difference in boiling-points of alcohol and ether, which, under the ordinary pressure, amounts to about 44° , from what is known with respect to the vapour-tension of these two substances at different temperatures, would, under the pressure of half an atmosphere, be above 45° , and below 40° under a pressure of three atmospheres.

From the observations at present at our disposal, it may be affirmed as a general rule, that in homologous compounds belonging to the same series, the differences in boiling-points are proportional to the differences of the formulæ. Exceptions obtain only in cases in which terms of a particular group are rather difficult to prepare, or when the substances boil at a very high temperature, at which the observations now at our command are for the most part uncertain. Again, it may be affirmed that the difference in boiling-points corresponding to the elementary difference $\text{C}_2 \text{ H}_2$, is in a great many series $= 19^\circ$; in some series more, in some series less.

There are a few quite exceptional cases in which the higher terms of a homologous series boil at a lower temperature than the inferior terms. A case in point exists according to WURTZ in the glycols.

TABLE XXII.

Ethyl-glycol	$\text{C}_4 \text{ H}_6 \text{ O}_4$	$197^\circ - 197.5^\circ$; Atkinson, 193° .
Propyl-glycol	$\text{C}_6 \text{ H}_8 \text{ O}_4$	188—189
Butyl-glycol	$\text{C}_8 \text{ H}_{10} \text{ O}_4$	183—184
Amyl-glycol	$\text{C}_{10} \text{ H}_{12} \text{ O}_4$	177

The ethers which arise from the combination of these bodies with acids $C_n H_n O_4$, exhibit on the other hand boiling-points rising with the increasing number of carbon-atoms. And this remark applies not only to those ethers of the glycols which contain two molecules of an acid-radical (compare Table XX.), but also to those in which only one of the two basic hydrogen-equivalents of ethyl-glycol is replaced by an acid-radical.

TABLE XXIII.

$C_8 H_8 O_6$	Monoacetate of Ethyl-glycol	Atkinson, 182°.
$C_{12} H_{12} O_6$	Monobutyrate of Ethyl-glycol	Lourenço, about 220°.
$C_{14} H_{14} O_6$	Monovalerate of Ethyl-glycol	Lourenço, about 240°.

One more example of a compound exhibiting a boiling-point lower than that of its lower homologue is offered by the cyanurates of methyl and ethyl. According to WURTZ's earlier experiments, cyanurate of methyl, $C_{12} H_9 N_3 O_6$, boils at 295°; according to a later observation, at 274°; cyanurate of ethyl, $C_{18} H_{15} N_3 O_6$, according to the earlier observation, at 276°; according to the later, at 253°. The boiling-points of the cyanic ethers, on the other hand, rise with the increase of the number of carbon-atoms; cyanate of methyl, $C_4 H_3 N O_2$ (boiling-point 40°, WURTZ), and cyanate of ethyl, $C_6 H_5 N O_2$ (boiling-point 60°, WURTZ), exhibit the difference of boiling-points usual in this kind of ethers.

Isomeric compounds belonging to the same type, and possessing the same chemical character, have the same boiling-point. This seems to follow from the boiling-points, such as have been observed for isomeric ethers $C_n H_n O_4$ (Table IV.); for ethers $C_n H_{n-8} O_4$ and $C_n H_{n-10} O_4$ (Table VII.); and for so-called simple and mixed radicals $C_n H_{n+2}$ (Table XIV.). Boiling-points, which at any rate very nearly approach each other, have also been observed for the isomeric ethers $C_n H_{n+2} O_2$ (see Table XVI.). For the isomeric ethers $C_n H_{n-2} O_8$, observation has hitherto yielded boiling-points which sometimes agree, sometimes differ. As yet no sufficient grounds exist for attributing different boiling-points to isomeric compounds of the same type and the same chemical character. It may sometimes be difficult experimentally to prove the identity of the boiling-point of two such compounds as an ethyl-ether and the isomeric methyl-compound. The methyl-compounds have in general so great a tendency to boil irregularly, and at temperatures anomalously raised, that quiet ebullition permitting the observation of the correct boiling-point is often scarcely to be attained.

Isomeric compounds belonging to the same type, but possessing a different chemical character, have different boiling-points. This is evident, *e. g.*, from a comparison of the acids and ethers $C_n H_n O_4$ (Tables III. and IV.); of the acids and ethers $C_n H_{n-2} O_4$, $C_n H_{n-8} O_4$, or $C_n H_{n-10} O_4$ (Tables VI. and VII.); of the alcohols and ethers $C_n H_{n+2} O_2$ (Tables II. and XVI.); of the mercaptans and the sulphur-compounds isomeric with them $C_n H_{n+2} S_2$ (Table XVIII.).

Isomeric compounds belonging to different types have different boiling-points. Allyl-

alcohol, $C_6H_6O_2$, boils (CAHOURS and HOFMANN) at 103° . (From Table V. this boiling-point was calculated at 107° .) Acetone, $C_6H_6O_2$, isomeric with the former, boils at 56° (LIEBIG, DUMAS, KOPP).

In cases like the last, the determination of the boiling-point of a compound, together with an examination of the substances with which the compound is serially allied in boiling-point, may be of great assistance in fixing its character, the type to which it belongs, and the series of homologous bodies of which it is a term. The examples just quoted of the fact that isomeric substances of different series possess different boiling-points, may here again serve as illustrations. The boiling-point of the so-called eugenic acid (BRÜNING, 248° ; WILLIAMS, 251°) shows that this substance, although represented by the formula $C_{20}H_{12}O_4$, cannot possibly be homologous to benzoic acid, $C_{14}H_6O_4$ (boiling-point observed by KOPP, 250° ; calculated, Table VI., 253°). This result might be inferred with the greatest probability from the boiling-point of the two substances, even if cuminic acid, isomeric with eugenic acid, and the homologue of benzoic acid, were not known. On the other hand, when the boiling-points of eugenic acid and of hydride of salicyl, $C_{14}H_6O_4$ (boiling-point 196° , PIRIA), are considered, it becomes extremely probable that these two bodies are homologous. (To the difference in composition, $C_6H_6=3C_2H_2$, corresponds in this case the difference in boiling-points $250-196=54=3 \times 18^\circ$.)

The boiling-points of polymeric compounds are also different, and may serve to determine the formula representing a substance.

Among the isomeric compounds, in the narrower sense of the word, acids and ethers (of the common formula $C_nH_nO_4$, for example), or alcohols and ethers (of the common formula $C_nH_{n+2}O_2$, *e. g.*), exhibit in all their bearings an essentially different character. Less striking is the difference of chemical character in the various volatile bases; and it is only since the last ten years that distinctive features have been traced in several classes of these bases, which have accordingly been subdivided into primary, secondary, and tertiary monamines. The basic character possessed by all these substances has induced many to compare their boiling-points also, without duly considering to which of the several classes they might belong. But in this case, again, a comparison of boiling-points is admissible only for such bases as belong to one and the same of the above-mentioned classes. The same formula, $C_{10}H_{13}N$, represents amylamine, propyl-ethylamine, and methyl-diethylamine; but of these three bases, only the first can be compared, as to boiling-point, with methylamine and ethylamine as a true homologue. The three isomeric bases above mentioned have indeed different boiling-points, just as ethyl-alcohol and methyl-ether, isomeric compounds (both $C_4H_6O_2$), have different boiling-points. We may, however, expect that methyl-propylamine and diethylamine, both isomeric bases of the same chemical character (both secondary monamines), will have the same boiling-point, just as in the case of the isomeric ethers of the same chemical character, propionate of methyl and acetate of ethyl.

Homologous bases of the common formula $C_nH_{n-5}N$ appear to exhibit, at least approximately, for a difference in the formulæ $=x C_2H_2$, a difference in boiling-points

$=x \times 19^\circ$. The temperatures of ebullition quoted in the following Tables under the head "assumed," thus calculated, pretty nearly coincide with the results of observation.

Primary monamines :

TABLE XXIV.

		Assumed.	Observed boiling-point.
C ₁₂ H ₇ N	... Aniline.....	179°	Hofmann, 182°; Kopp, 185°.
C ₁₄ H ₉ N	... Toluidine.....	198	Muspratt and Hofmann, 198°.
C ₁₆ H ₁₁ N	... Xylidine.....	217	Church, 213°—214°.
C ₁₈ H ₁₃ N	... Cumidine.....	236	Nicholson, 225°.
C ₂₀ H ₁₅ N	... Cymidine.....	255	Barlow, about 250°.

Secondary monamines :

TABLE XXV.

		Assumed.	Observed boiling-point.
C ₁₄ H ₉ N	... Methyl-aniline.....	185°	Hofmann, 192°.
C ₁₆ H ₁₁ N	... Ethyl-aniline.....	204	Hofmann, 204°.
C ₁₈ H ₁₃ N	... Ethyl-toluidine.....	223	Morley and Abel, 217°.
C ₂₀ H ₁₅ N	242	
C ₂₂ H ₁₇ N	... Amyl-aniline.....	261	Hofmann, 258°.

Tertiary monamines :

TABLE XXVI.

		Assumed.	Observed boiling-point.
C ₁₀ H ₅ N	... Pyridine.....	115°	Anderson, 115°.
C ₁₂ H ₇ N	... Picoline.....	134	Anderson, 135°.
C ₁₄ H ₉ N	... Lutidine.....	153	Anderson, 154°; Williams, 160°—165°.
C ₁₆ H ₁₁ N	... Collidine.....	172	Anderson, 179°; Williams, 179°—182°.
C ₁₈ H ₁₃ N	191	
C ₂₀ H ₁₅ N	... Diethyl-aniline.....	210	Hofmann, 213°·5.
C ₂₂ H ₁₇ N	... Diethyl-toluidine.....	229	Morley and Abel, 229°.
C ₂₄ H ₁₉ N	248	
C ₂₆ H ₂₁ N	... Ethyl-amyl-aniline.....	267	Hofmann, 262°.

The isomeric bases C_nH_{n-5}N, belonging to different classes, have different boiling-points. The discrepancies are by no means great in the case of the isomeric terms of the primary and secondary monamines, but considerable enough in the case of the tertiary monamines compared with the two previous classes, so that the bases belonging to the third class may be distinctly recognized. Dimethylaniline may be expected to exhibit the same boiling-point as collidine, isomeric with it, and likewise a tertiary monamine.

The relation mentioned (page 261), viz. that for certain classes of alcohols, acids and ethers, a boiling-point $x \times 14^{\circ} \cdot 5$ higher or lower corresponds to x C more or less in the formula, is in general not observed on comparing the bases of the first and second class; but the boiling-points of a large number of tertiary monamines, such as they are calculated from the (assumed) boiling-points of the last Table, coincide tolerably well with the results of observation.

TABLE XXVII.

		Calculated.	Observed boiling-point.
$C_{12}H_{18}N$... Methyl-piperidine	104	Cahours, 117°.
$C_{14}H_{16}N$... Ethyl-piperidine	123	Cahours, 128°.
$C_{20}H_{21}N$... Amyl-piperidine	180	Cahours, 186°.
$C_{16}H_{19}N$... Methyl-ethyl-amylamine.....	132	Hofmann, 135°.
$C_{18}H_{21}N$... Diethyl-amylamine	151	Hofmann, 154°.
$C_{30}H_{38}N$... Triamylamine	265	Hofmann, 257°.

Accordingly in the last two series also the difference in boiling-point (19°) seems, at all events approximately, to correspond to the elementary difference C_2H_2 . We meet, however, with an exception in the boiling-point of trimethylamine, C_6H_9N , a base likewise belonging to the tertiary monamines, which, according to WINKLES, lies between 4° and 5° .*

The general formula $C_nH_{n+3}N$ represents volatile bases of the three classes. What is known with regard to the boiling-points of the tertiary monamines has already been stated. With respect to the secondary, HOFMANN'S determination of the boiling-points of diethylamine, $C_8H_{11}N$, = $57^\circ.5$, of diamylamine, $C_{20}H_{23}N$, = about 170° , also exhibits for the difference of composition $x C_2H_2$, a difference in boiling-points of 19° ($170 - 57 = 6 \times 19^\circ$). The difference is greater for the primary bases $C_nH_{n+3}N$; the boiling-points assumed in the following Table are based on the supposition that it equals 25° .

TABLE XXVIII.

		Assumed.	Observed boiling-point.
C_2H_5N	... Methylamine	- 6	Wurtz, about 0° .
C_4H_7N	... Ethylamine	+ 19	Wurtz, 19° .
C_6H_9N	44	
$C_8H_{11}N$... Butylamine	69	Wurtz, $69^\circ - 70^\circ$.
$C_{10}H_{13}N$... Amylamine	94	Brazier and Gossleth, 93° ; Wurtz, 95° .
$C_{12}H_{15}N$	119	
$C_{14}H_{17}N$	144	
$C_{16}H_{19}N$... Caprylamine	169	Squire, 164° ; Cahours, $172^\circ - 175^\circ$.

In the case of the bases $C_nH_{n+3}N$, it does not appear that the isomeric terms belonging to the classes of secondary and tertiary monamines can be distinguished by means

* The trimethylamine used by M. WINKLES, in determining the boiling-point, had been prepared from the brine of salted herrings. Whilst Professor KOPP'S paper was passing through the press, I had an opportunity of determining the boiling-point of perfectly pure trimethylamine, prepared by the action of potassa on iodide of tetramethylammonium. This determination, made with about 10 grms. of base, gave the boiling-point $9^\circ.3$. The ebullition of trimethylamine exhibits the irregularity so frequently observed in methyl-compounds. When the liquid ceases to boil freely, the thermometer is observed to indicate as much as 14° and even 15° , but the mercury falls again suddenly to $9^\circ.3$, when ebullition recommences. It deserves to be noticed, that trimethylphosphine exhibits a similarly discrepant boiling-point. The boiling-point of trimethylphosphine was found between 40° and 42° , that of triethylphosphine being $127^\circ.5$.—A. W. H.

of their boiling-points; but the boiling-points of the primary monamines greatly differ from those of the isomeric bases of the two previous classes.

Constant relations then between the boiling-points and the formulæ of the volatile organic compounds may be said to have been most positively established by the preceding statements. Their existence cannot be called in question on account of their not always being manifested exactly in the same manner. Such uniformity would obtain if in all homologous series the difference in boiling-points corresponding to the difference of composition $C_2 H_2$ were equally great; if, as a general rule, on comparing two corresponding pairs of compounds the same difference in composition were found to involve the same difference in boiling-point. The fact of these relations obtaining in a less general and simple manner renders their perception, as also their use in determining the formulæ of chemical compounds, more difficult, but does not set them aside, any more than the existence of a relation between chemical composition and crystalline form could be denied, on account of its not always manifesting itself in the simplest form, or the assistance be doubted, which the study of crystalline form often renders in establishing the formula of a substance, because compounds of altogether different atomic constitution may possess the same form, or compounds of analogous constitution, even containing so-called isomorphous elements, are observed to crystallize in forms altogether different.

Relations between boiling-point and composition have been more especially proved in organic compounds; very many of them, being volatile at comparatively low temperatures, admit of their boiling-point being accurately determined. It is, however, in the nature of the case that they should not be limited to the domain of organic chemistry. Nevertheless relations of this description have not hitherto been comprehensively proved to exist in inorganic bodies. Tribromide of arsenic, $As Br_3$ (boiling-point 220°), and trichloride of arsenic, $As Cl_3$ (133°), exhibit nearly the same difference as oxybromide of phosphorus, $PO_2 Br_3$ (195°), and oxychloride of phosphorus, $PO_2 Cl_3$ (110°), and also nearly the same as the following organic compounds (exhibiting a similar difference in their formulæ), bromoform, $C_2 H Br_3$ (152°), and chloroform, $C_2 H Cl_3$ (62°). In these cases the substitution of 3 Br for 3 Cl is attended by an elevation of the boiling-point amounting to from 85° to $90^\circ = 3 \times 28$ to 3×30 . But the substitution of x Br for x Cl by no means involves invariably an elevation of the boiling-point of from $x 28^\circ$ to $x 30^\circ$. Although earlier observations had pointed to these simple relations, and raised the hope that a knowledge of the differences in the boiling-points of corresponding bromine and chlorine compounds would be available for ascertaining how many equivalents of bromine in a substance are substituted for chlorine in another, yet the determination of the boiling-points of a very large number of corresponding bromine and chlorine compounds has unmistakably shown that so simple a relation does not obtain, and cannot therefore throw any light upon the formulæ of such substances.

The recognition then of definite relations between composition and boiling-point is for the present chiefly limited to organic compounds. For the majority of these com-

pounds, and indeed for the more important ones, this relation assumes the form of a simple law, which, more especially for the monatomic alcohols $C_n H_m O_2$, for the monobasic acids $C_n H_m O_4$, and for the compound ethers $C_n H_m O_4$, generated by the union of the two previous classes, is proved in the most general manner; so much so, indeed, that in many cases the determination of the boiling-point furnishes most material assistance in fixing the true character and position of a compound. And it deserves more especially to be noticed, that the simplest and most comprehensive relations have been recognized for those classes of organic compounds which have been longest known and most accurately investigated; and that even for those classes, the generality and simplicity of the relation, on account of numerous boiling-points incorrectly observed at an earlier date, appeared in the commencement doubtful, and could be more fully acknowledged only after a considerable number of new determinations. Thus we are justified in hoping that in other classes also of compounds in which simple and comprehensive relations have not hitherto been traced, these relations will become perceptible as soon as the verification of the boiling-points of terms already known, and the examination of new terms, shall have laid a broader foundation for our conclusions.